

| L Number | Hits | Search Text | DB | Time stamp |
|----------|------|--|---|------------------|
| 1 | 1 | 6235358.pn. | USPAT; US-PGPUB | 2004/03/22 13:10 |
| 2 | 1 | 5077174.pn. | USPAT; US-PGPUB | 2004/03/22 13:29 |
| 3 | 317 | victoria adj green | USPAT; US-PGPUB | 2004/03/22 13:32 |
| 4 | 0 | (victoria adj green) near5 sensitizer | USPAT; US-PGPUB | 2004/03/22 13:32 |
| 5 | 1 | (victoria adj green) same sensitizer | USPAT; US-PGPUB | 2004/03/22 13:34 |
| 6 | 1856 | benzophenone same sensitizer | USPAT; US-PGPUB | 2004/03/22 13:34 |
| 7 | 631 | benzophenone near5 sensitizer | USPAT; US-PGPUB | 2004/03/22 13:43 |
| 8 | 0 | jp-6235358-\$.did. | USPAT; US-PGPUB; EPO; JPO; DERWENT | 2004/03/22 13:44 |
| 9 | 1 | jp-11140110-\$.did. | USPAT; US-PGPUB; EPO; JPO; DERWENT | 2004/03/22 13:48 |
| 10 | 0 | jp-06235358-\$.did. | USPAT; US-PGPUB; EPO; JPO; DERWENT | 2004/03/22 13:49 |
| 11 | 2 | jp-60235358-\$.did. | USPAT; US-PGPUB; EPO; JPO; DERWENT | 2004/03/22 13:57 |
| 13 | 0 | (imidosulfonate or imidesulfonate) same sensitizer | USPAT; US-PGPUB; EPO; JPO; DERWENT | 2004/03/22 13:58 |
| 15 | 0 | (\$2hydroxyimidosulfonate) same sensitizer | USPAT; US-PGPUB; EPO; JPO; DERWENT | 2004/03/22 13:59 |
| 12 | 2 | (oxime adj sulfonate) same sensitizer | USPAT; US-PGPUB; EPO; JPO; DERWENT | 2004/03/22 13:59 |
| 14 | 2 | (\$2oxyimidosulfonate) same sensitizer | USPAT; US-PGPUB; EPO; JPO; DERWENT | 2004/03/22 14:00 |



US006235358B1

(12) **United States Patent**
Goto et al.

(10) **Patent No.:** US 6,235,358 B1
(45) **Date of Patent:** May 22, 2001

(54) **PACKAGE CONTAINER AND CONTAINER CLOSURE**

(75) **Inventors:** Hiroaki Goto; Hiroshi Sasaki, both of Tokyo (JP)

(73) **Assignee:** Toyo Seikan Kaisha, Ltd., Tokyo (JP)

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) **Appl. No.:** 09/136,616

(22) **Filed:** Aug. 20, 1998

(51) **Int. Cl.⁷** B32B 27/38

(52) **U.S. Cl.** 428/35.7; 522/25; 522/31; 428/35.8; 428/413

(58) **Field of Search** 522/25, 31; 428/34.4, 428/34.5, 35.2, 35.3, 35.8, 36, 35.7, 66.3, 412, 413, 457

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,554,770 * 1/1971 Lipsky et al. 99/174
4,058,401 * 11/1977 Crivello 96/115 R
4,287,228 * 9/1981 Schlesinger 427/54.1
4,624,912 * 11/1986 Zweifel et al. 430/258
4,704,310 * 11/1987 Tighe et al. 427/261
5,731,123 * 3/1998 Kawamura et al. 430/176

FOREIGN PATENT DOCUMENTS

96-7344 6/1996 (JP) C09D/163/00

OTHER PUBLICATIONS

Aizawa et al., Derwent Abstract ZA 8207142A.*

* cited by examiner

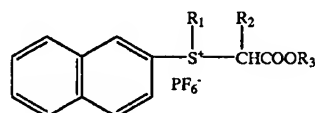
Primary Examiner—Rena L. Dye

Assistant Examiner—Sow-Fun Hon

(74) **Attorney, Agent, or Firm**—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

(57) **ABSTRACT**

This invention related to a packaging container and a container closure having excellent curability, aesthetic beauty of an ultraviolet ray hardened coating, transferability of a container, heat-resistant treatability, retortability, and sanitary characteristics. The present invention provides to a packaging container and a container closure having, on the outer surface, a coating layer of a resin composition which comprises a cationic curable resin comprising an alicyclic epoxy resin, a photo-cationic-curing catalyst comprising a compound of the following formula (1),



wherein each of R₁ and R₂ is an alkyl group, and they may be the same or different, and R₃ is an alkyl group, a sensitizer comprising a thioxanthone sensitizer,

and a pigment comprising titanium dioxide, wherein the amount of said titanium dioxide is at least 0.30 mg per 1 cm² of said coating layer, the amount of said photo-cationic-curing catalyst is 1 to 20% by weight with regards to said titanium dioxide, and the amount of said sensitizer is 1.5 to 5% by weight with regards to said titanium dioxide.

9 Claims, No Drawings

PACKAGE CONTAINER AND CONTAINER CLOSURE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a packing container and a container closure having a coating layer or a printing ink layer of an ultraviolet ray-curable resin on an outside surface, and more specifically, to a packaging container and a container closure having excellent curability, aesthetic beauty of an ultraviolet ray hardened coating, transferability of a container, heat-resistant treatability, retortability, and sanitary characteristics.

2. Prior Art

An ink or coating composition containing an ultraviolet-curable resin does not have a problem of the volatilization of a solvent in drying or baking. Furthermore, since a printed matter or a coated product does not need heating, these compositions are used in various applications or such a use have been investigated.

As examples of heretofore used ultraviolet ray-curable resin compositions, a combination of an epoxy resin and a cationic ultraviolet ray polymerization initiator, a combination of urethane (meth)acrylate and an acrylate monomer, and an epoxy (meth)acrylate resin have been known.

Japanese technical Publication No. 7344/96 (Published on Jul. 3, 1996; Nippon Unicar Co.; developer: Eiji Ando and Kenichi Suzuki; Int.Cl. C09D163/00) describes a resin composition composed of an ultraviolet-curable resin composition comprising an aliphatic cyclic epoxy resin, a cationic polymerization initiator, and polydiorganosiloxane-polyoxyalkylene alternate block copolymer.

An ultraviolet-curable resin composition contains an photo-cationic-polymerizable epoxy-type monomer and an photo-cationic-polymerization initiator has an advantage of forming a cured coating by ultraviolet irradiation without the need of heating. However, the ultraviolet-cured coating to be formed has an insufficient degree of curing, and as a coating layer or a printing ink layer of a package container, it has an insufficient problem in transferability, heat-resistant treatability and retortability. In this packaging container, a smooth transferring operation of a container is essential in a production step and a filling step. If the degree of curing is low in the coating layer or in the printing ink layer or slidability is poor on the outer surface, the coating will be easily damaged by contact with another object or by collision with another object. Furthermore, to improve the preservability of the contents, hot filling, sterilization by pasteurizer and retort sterilization have been carried out, but known ultraviolet ray-curable resins which can withstand these heat treatments, especially retort sterilization operation, are very few.

The photo-cationic-curing catalysts are decomposed by ultraviolet rays and release Lewis acid. This Lewis acid polymerizes an epoxy group, and for example, an aromatic iodonium salt, an aromatic sulfonium salt, an aromatic selenium salt and an aromatic diazonium salt are used. However, although these photo-cationic-curing catalysts have a satisfactory sensitivity to ultraviolet rays having a short wavelength of generally 280 nm or below, they do not have a sufficient sensitivity to ultraviolet rays having a long wavelength. They only can insufficiently satisfy a purpose of forming the coating layer or the printing ink layer of the containers by curing due to ultraviolet rays. The pigments contained in the coating layer or the printing ink layer absorb

ultraviolet rays having a short wavelength, for example, titanium dioxide absorbs ultraviolet rays having a shorter wavelength than 380 nm.

Furthermore, the photo-cationic-curing catalysts have a problem of sanitary characteristics. Known photo-cationic-curing catalysts may have a toxicity, and an iodonium salt has a problem of irritability of a bodily part. Furthermore, antimonate has a problem because it is composed of a heavy metal salt.

Of course, these photo-cationic-curing catalysts may be used in combination with known sensitizers, but many of the sensitizers have a problem of toxicity. Such sensitizers might not show a sensitizing action on ultraviolet rays having a long wavelength. Furthermore, some sensitizer may have a strongly brown color and may color the cured coated film. Combinations of photo-cationic-curing catalysts showing satisfactory curing properties to ultraviolet rays on the long wavelength with sensitizers have not been known so much.

SUMMARY OF THE INVENTION

The present inventors have found that a combination of a photo-cationic-curing catalyst composed of a specified sulfonium salt with a thioxanthone-type sensitizer shows satisfactory curing properties to ultraviolet rays having a long wavelength without generating the above-mentioned defects even when a pigment of titanium dioxide is contained in a high optical concentration, a coating layer or a printing ink layer having excellent curability, aesthetic beauty, transferability of a container, heat treatability, retortability, and sanitary characteristics can be formed on a packaging container or a container closure.

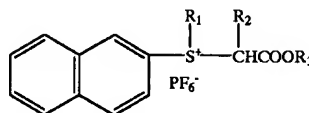
It is an object of this invention to provide a packaging container and a container closure having an ultraviolet-curable coating layer or a printing ink layer having excellent curability, aesthetic beauty, transferability of a container, heat treatability, retortability, and sanitary characteristics, the above coating layer or the printing ink layer showing satisfactory curing properties on ultraviolet rays having a long wavelength.

According to this invention, there are provided a packaging container and a container closure having, on the outer surface, a coating layer of a resin composition which comprises

a cationic curable resin comprising an aliphatic cyclic epoxy resin.

a photo-cationic-curing catalyst comprising a compound of the following formula (1),

(1)



wherein each of R₁ and R₂ is an alkyl group, and they may be the same or different, and R₃ is a hydrogen atom or an alkyl group,

a sensitizer comprising a thioxanthone sensitizer, and

a pigment comprising titanium dioxide,

wherein;

the amount of said titanium dioxide is at least 0.3 mg, especially 0.4 to 0.9 mg, per 1 cm² of said coating layer,

the amount of said photo-cationic-curing catalyst is 1 to 20%, especially 1.5 to 10%, by weight with regard to said titanium dioxide, and

3

the amount of said sensitizer is 1.5 to 5%, especially 1.5 to 4% by weight with regards to said titanium dioxide.

1. The photo-cationic-curing catalysts include 2-naphthyl-1-ethoxycarbonylethylmethyl sulfonium hexafluorophosphonate (catalyst 1), 2-naphthyl-1-methoxycarbonylethylmethyl sulfonium hexafluorophosphonate (catalyst 2) and 2-naphthyl-1-ethoxycarbonylpropylmethyl sulfonium hexafluorophosphonate (catalyst 3).

2. The above resin composition contains 1 to 20 parts by weight, especially 1.5 to 10 parts by weight, of the photo-cationic-curing catalyst, and 1.5 to 5 parts by weight, especially 1.5 to 4 parts by weight, of the thioxanthone-type sensitizer, per 100 parts by weight of titanium dioxide.

3. The above resin composition contains 30 to 250 parts by weight, especially 40 to 220 parts by weight, of titanium dioxide, especially rutile-type titanium dioxide, per 100 parts by weight of the alicyclic epoxy resin.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT OF THE INVENTION

The container of this invention may be any packaging container or any container closure formed from a metal, a plastic or a laminate thereof, such as a can or a closure composed of a metal material or a coated metal material, a bottle or a closure composed of a thermoplastic resin, or a pouch or a closure composed of a thermoplastic resin laminate or a thermoplastic resin-metal foil laminate.

In this invention, a specified sulfonium salt of the above formula (1) is selected as the photo-cationic-curing catalyst, and is combined with the thioxanthone-type sensitizer, the alicyclic epoxy resin and the titanium dioxide pigment to use the combination in forming the coating layer or the printing ink layer of the package or closure.

The sulfonium salt used in this invention is structurally characterized in that the aryl group bonded to a sulfur atom is a 2-naphthyl group, a 1-alkoxycarbonylalkyl group is bonded to the sulfur atom, and moreover, the coordinated anion of the sulfonium salt is a hexafluorophosphonate anion.

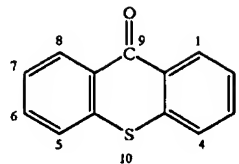
This sulfonium salt shows excellent dissolvability and dispersibility in the alicyclic epoxy resin composition and also shows excellent curability in a combination with the below-mentioned thioxanthone-type sensitizer, especially excellent curability under conditions in which ultraviolet rays shorter than 380 nm are absorbed by the pigment, and the formed film is not injured during transferring the package container, and under retorting sterilization conditions, the formed film does not feel rough nor becomes whitened nor forms a blister, and the film has excellent heat resistance and hot water resistance.

The sulfonium salt has excellent sanitary characteristics. The results of a Ames test are negative with respect to the above-mentioned catalysts 1 to 3.

The thioxanthone-type sensitizer used in this invention has a skeleton shown in the following formula (2)

4

(2)



and gives an excellent sensitization effect in combination with a specified sulfonium salt, especially gives an excellent sensitization effect under conditions in which ultraviolet rays shorter than 380 nm are absorbed by the pigment. As already pointed out, many of the sensitizers have a yellow brown color, and the cured film is colored. However, this thioxanthone-type sensitizer colors a cured film comparatively seldom, and gives an excellent outer appearance of the cured film, and can increase the merchandize value of the package. Furthermore, the thioxanthone-type sensitizer has excellent sanitary characteristics among various sensitizers.

As stated above, a specified sulfonium salt-type photo-cationic-curing catalyst is combined with the thioxanthone-type sensitizer and the alicyclic epoxy resin, and by compounding the combined compounds in a coating layer or a printing ink layer of the package container, these compounds show satisfactory curing properties against ultraviolet rays having a long wavelength without showing the defects of the conventional technology. As a result, it is possible to form a coating layer or a printing ink layer having excellent curability, aesthetic beauty of a film cured by ultraviolet rays, transferrability of the container, heat treatment resistance, retortability, and sanitary characteristics on a package container.

In this invention, even when the amount of titanium dioxide is as large as at least 0.30 mg/cm² with regards to the unit area of the coating layer, a combination of the sulfonium salt-type curing catalyst and the thioxanthone-type sensitizer can give an excellent curing action by ultraviolet rays.

As described above, titanium dioxide contained in the ultraviolet-curable resin composition absorbs ultraviolet rays having a shorter wavelength than 380 nm, and retards the curing of the resin. In contrast, in spite of the fact that in the resin composition of this invention, the optical concentration of titanium dioxide is relatively high, the curing of the resin composition is carried out sufficiently by UV irradiation within a short period of time. Since the TiO₂ concentration is high, a satisfactory whiteness can be obtained. Furthermore, intimate adhesiveness or abrasion resistance of a coating substrate is increased, and a metallic container or closure has increased corrosion resistance. The above-mentioned advantage is obtained by compounding titanium dioxide in the resin composition. Especially, from the standpoint of aesthetic beauty of the container, the titanium dioxide have a relatively high optical concentration of 0.30 to 1.0 mg/cm² per unit area of the coating layer. If the amount of titanium dioxide per unit area of the coating layer is lower than the above range, an excellent outer appearance cannot be obtained, and on the other hand, if the amount of titanium dioxide exceeds the above range, there is no extreme change in hiding power nor a particular advantage.

To obtain UV curability within a short period of time, the photo-cationic-curing catalyst should be used in an amount of 1 to 20% by weight, especially in an amount of 1.5 to 10% by weight with regards to the titanium dioxide. On the other hand, the amount of the sensitizer per titanium dioxide

5

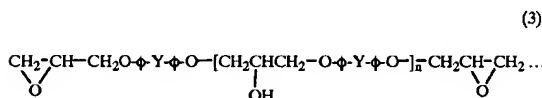
should be 1.5 to 5% by weight, especially 1.5 to 4% by weight. When the amount of the sensitizer is lower than the above range, UV curability tends to be decreased. On the other hand, if the amount of the sensitizer is larger than the above range, the hardened resin layer tends to be colored in a color phase inherent to the sensitizer, namely a yellow color.

[Photo-cationic-polymerizable Epoxy Resin]

The photo-cationic-polymerizable epoxy resin includes an epoxy resin component having an alicyclic group in the molecule in which a carbon atom adjacent to the alicyclic group forms an oxirane ring. For example, epoxy compounds having at least one epoxycycloalkane group within the molecule such as an epoxycyclohexane ring or an epoxycyclopentane ring are used singly or as mixtures.

Suitable examples include vinylcyclohexene diepoxide; vinylcyclohexene monoepoxide; 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-m-dioxane; bis(3,4-epoxycyclohexyl)adipate; and limonen dioxide.

In the present invention, the above alicyclic epoxy resins may be used singly or as mixtures of at least two resins, or with another epoxy resin. Other epoxy resins are general-purpose resins derived from polyvalent phenols such as bisphenols and epihalohydrins. A epoxy resin composed of repeating units expressed by the formula (3)



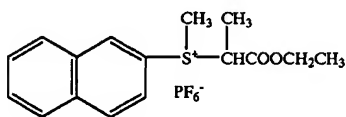
wherein ϕ is a phenylene group, and Y is a bridging group such as a methylene group, an ethylidene group or a 2,2-propylidene group. This epoxybisphenol-type resin preferably has an epoxy equivalent of 3000 to 5500, and a number average molecular weight of 3500 to 5000.

In the epoxy resin used in this invention, the alicyclic epoxy resin component accounts for at least 70% by weight, especially at least 80% by weight, of the total epoxy resin preferably in respect of the curability of ultraviolet rays.

[Photo-cationic-curing Catalyst]

In this invention, as the photo-cationic-curing catalyst, the sulfonium salt expressed by general formula (1) is used. In general formula (1), examples of the alkyl groups R_1 , R_2 and R_3 are alkyl groups having not larger than 4 carbon atoms, such as a methyl group, an ethyl group, a propyl group and a butyl group. R_1 is preferably a methyl group; R_2 is preferably a methyl group or an ethyl group; and R_3 is preferably a methyl group or an ethyl group.

Especially preferred sulfonium salts include a 2-naphthyl-1-ethoxycarbonyl ethylmethylsulfonium hexafluorophosphate (catalyst 1), namely the following formula (4), namely a sulfonium salt expressed by the following formula (4)

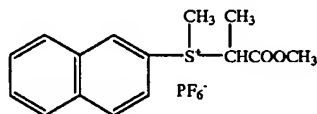


(4) 60 wherein R_4 , R_5 , R_6 and R_7 may be the same or different and represent a hydrogen atom, an alkyl group or a chlorine atom.

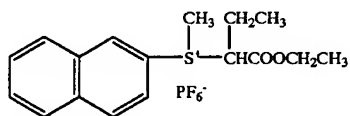
Specific compounds include 2,4-diethylthioxanthone, 2-isopropylthioxanthone, 4-isopropylthioxanthone, 1-chloro-4-propoxythioxanthone, and mixtures thereof. The present invention is of course not limited to these examples.

6

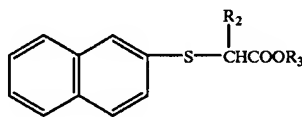
a 2-naphthyl-1-methoxycarbonyl ethylmethylsulfonium hexafluorophosphate (catalyst 2), namely a sulfonium salt expressed by the following formula (5)



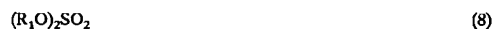
2-naphthyl-1-ethoxycarbonylpropylmethylsulfonium hexafluorophosphate (catalyst 3), namely a sulfonium salt expressed by the following formula (6)



The above sulfonium salts used in this invention can be obtained by reacting 2-naphthyl-1-alkoxycarbonylalkyl sulfide expressed by the following formula (7)



wherein R_2 and R_3 are as defined above, with a dialkylsulfuric acid expressed by the following formula (8)

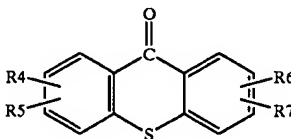


wherein R_1 is as defined above, and reacting the reaction product with potassium phosphate 6-fluoride.

[Thioxanthone-type Sensitizers]

Sensitizers used in this invention are known compounds having a thioxanthone skeleton, and any thioxanthone-type compounds may be used.

Preferred thioxanthone-type sensitizers are compounds of the following formula (9)



(9) 60 wherein R_4 , R_5 , R_6 and R_7 may be the same or different and represent a hydrogen atom, an alkyl group or a chlorine atom.

Specific compounds include 2,4-diethylthioxanthone, 2-isopropylthioxanthone, 4-isopropylthioxanthone, 1-chloro-4-propoxythioxanthone, and mixtures thereof. The present invention is of course not limited to these examples.

[Ultraviolet-curable Resin Compositions]

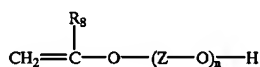
The ultraviolet-curable resin composition used in this invention may include the alicyclic epoxy resin, the specified sulfonium salt-type photo-cationic-curing catalyst, the thioxanthone-type sensitizer and titanium dioxide as essential components.

It is preferred that the specified sulfonium salt-type photo-cationic-curing catalyst is used in an amount of 1 to 20 parts by weight, especially in an amount of 1.5 to 10 parts by weight, per 100 parts by weight of titanium dioxide. If the amount of the sulfonium salt-type photo-cationic-curing catalyst is below the above range, sufficient ultraviolet curability cannot be obtained. On the other hand, when the amount of the sulfonium salt-type photo-cationic-curing catalyst exceeds the above range, no particular advantage is obtained. Economically, it is disadvantageous, and the catalyst residue will cause adverse effects.

On the other hand, the thioxanthone-type sensitizer may be used in an amount of 1.5 to 5 parts by weight, especially in an amount of 1.5 to 4 parts by weight, per 100 parts by weight of titanium dioxide. If the amount of the thioxanthone-type sensitizer is below the above-mentioned range, sufficient ultraviolet curability cannot be obtained. On the other hand, if the amount of the thioxanthone-type sensitizer exceeds the above range, no particular advantage can be obtained. Economically, it becomes disadvantageous, and excessive sensitizer tends to cause coloration of the film.

The ultraviolet ray-curable resin composition used in this invention may contain a cross-linking agent, a crosslinking promotor, a reactive diluent, a plasticizer, a lubricant, a levelling agent and a pigment such as titanium dioxide according to known recipes.

In the ultraviolet ray-curable resin composition used in this invention, especially in a composition used as a coating layer, a hydroxyl-containing ethylenically unsaturated monomer, especially a monomer expressed by the formula (10)



wherein R_8 is a hydrogen atom or a lower alkyl group, Z is an alkylene group having 2 to 6 carbon atoms, and n is a number of at least 1, may be added as a cross-linking agent also serving as a diluent.

With respect to cationic polymerizability, the hydroxyl-containing ethylenically unsaturated monomer is preferably a monomer having an ether group bonded to the ethylenically unsaturated carbon atom, more specifically, a monomer expressed by the general formula (10). This chemical structure imparts high cationic polymerization activity, and give a pliable structure composed of an aliphatic ether linkage.

In the general formula (10), the alkylene group may be a straight chain alkylene group or a branched chain alkylene group. The number of n is not particularly limited, but preferably may be a number of 4 or below. Examples of this monomer may include 4-hydroxybutyl ether, 1,6-hexanediol monovinyl ether, neopentyl glycol monovinyl ether, ethylene glycol monovinyl ether, diethyleneglycol monovinyl ether, triethylene glycol monovinyl ether, dipropylene glycol monovinyl ether, tripropylene glycol monovinyl ether, dibutylene glycol monovinyl ether, tributylene glycol monovinyl ether, pentaerythritol divinyl ether, trimethylol propane monovinyl ether, trimethylol propane divinyl ether, pentaerythritol monovinyl ether and dipentaerythritol divinyl ether.

The hydroxyl-containing ethylenically unsaturated monomer may be used in an amount of 2 to 30 parts by weight, especially in an amount of 5 to 20 parts by weight, per 100 parts by weight of the alicyclic epoxy resin.

Examples of other reactive diluents include polyvalent alcohol derivatives and oxetane compounds. The polyvalent alcohol derivatives may contain at least one known hydroxyl group. Examples of the oxetane compounds are 3-ethyl-3-phenoxy methyloxetane, 3-methyl-3-hydroxymethyloxetane, and 3-ethyl-hydroxymethyloxetane. These polyvalent alcohol derivative or the oxetane compounds are used preferably in an amount of 1 to 15 parts by weight, especially in an amount of 2 to 10 parts by weight, per 100 parts by weight of the alicyclic epoxy resin.

Other examples of the cross-linking agent include resins containing an epoxy group within the molecule such as epoxidized polybutadiene and resins containing a hydroxyl group in the molecule. These resin-type cross-linking agents can be used in an amount of 2 to 30 parts by weight, especially 5 to 20 parts by weight, per 100 parts by weight of alicyclic epoxy resin.

The organic silicone-type resin used as an arbitrary component in this invention may be any desired organic silicone-type resins if they impart levelling property to the formed ultraviolet ray-cured resin layer and slidability to ultraviolet ray cured resin film. Preferred examples of the organic silicone-type resins include polyalkylhydrogen siloxanes containing alkyl groups containing 1 to 18 carbon atoms, especially alkyl (7 to 8 carbon atoms) modified products of polymethylhydrogen siloxanes.

As organic silicone-type resins, polyorganosiloxane-polyoxyalkylene block copolymers described in the above-mentioned Japanese technical Publication described above may be used.

The organic silicone resins may be used in an amount of 0.05 to 2 parts by weight, especially 0.1 to 1 part by weight, per 100 parts by weight of the alicyclic epoxy resin.

Pigments used in inks and paints may be those comprising of titanium dioxide as a main component but not limited to these materials.

Even pigments which cause curing obstruction may be used sufficiently if these pigments are coated.

Black Pigments

Carbon black, acetylene black, lamp black and aniline black.

Yellow Pigments

Chrome yellow, zinc yellow, cadmium yellow, yellow iron oxide, mineral fast yellow, nickel titanium yellow, naples yellow, naphthol yellow S, Hansa Yellow G, Hansa Yellow 10G, Benzidine Yellow G, Benzidine Yellow GR, quinoline yellow lake, Permanent Yellow NCG, and Tartrazine Lake.

Orange Pigments

Chrome orange, molybdenum orange, Permanent Orange GTR, pyrazolone orange, Vulcan Orange, Indanthrene Brilliant Orange RK, Benzidine Orange G, and Indanthrene Brilliant Orange GK.

Red Pigments

Red iron oxide, cadmium red, red lead, cadmium mercury sulfide, Permanent Red 4R, Lithol Red, pyrazolone red, Watchung Red Calcium Salt, Lake Red D, Brilliant Carmine 6B, eosine lake, Rhodamine Lake B, Alizarine Lake and Brilliant Carmine 3B.

Violet Pigments

Manganese violet, Fast Violet B, and methyl violet lake.

Blue Pigments

Prussian Blue, cobalt blue, alkali blue lake, Victoria blue lake, phthalocyanine blue, non-metallic phthalocyanine

blue, partially chlorinated phthalocyanine blue, Fast Sky Blue and Indanthrene Blue BC.

Green Pigments

Chrome green, chromium oxide, Pigment Green B, malachite green lake and Final Yellow Green G.

White Pigments

Zinc white, antimony white and zinc sulfide.

Extender Pigments

Baryta powder, barium carbonate, clay, silica, white carbon, talc and alumina white.

The above pigments may be used in an amount of 200 parts by weight or below, especially 180 parts by weight or below per 100 parts by weight of the resin composition.

A lubricant may be compounded in the ultraviolet ray-curable resin composition to impart slidability to an outside surface.

Examples of the lubricant include (a) hydrocarbon-type compounds such as flowing, natural or synthetic paraffins, microwaxes, polyethylene waxes, and chlorinated polyethylene waxes; (b) aliphatic acid compounds such as stearic acid and lauric acid; (c) aliphatic acid monoamide-type compounds or bisamide-type compounds such as stearamide, palmitamide, oleamide, esilic acid amide, methylenebisstearamide, and ethylenebisstearamide; (d) ester-type compounds such as butyl stearate, hardened castor oil and ethylene glycol monostearate; (e) alcohol-type compounds such as cetyl alcohol and stearyl alcohol; (f) metal soaps such as zinc stearate, magnesium stearate and calcium stearate; and (g) mixtures of the above compounds.

These lubricants may be used in an amount of 10 parts by weight or below, especially 2 to 8 parts by weight, per 100 parts by weight of the resin composition.

A plasticizer may be contained in the ultraviolet ray-curable resin composition to impart flexibility or pliability to the coated film. Examples of the plasticizer include ester-type plasticizers such as phthalic acid ester-type plasticizers, adipic acid ester-type plasticizers and succinic acid ester-type plasticizers; polyester-type plasticizers, phosphoric ester-type plasticizers and chlorine-type plasticizers.

These plasticizers may be used in an amount of 15 parts by weight or below, especially 1 to 10 parts by weight, per 100 parts by weight of the resin composition.

Since the ultraviolet ray-curable resin composition used in this invention shows a marked non-Newtonian behavior, it is difficult to define its viscosity. But a shearing speed at an apparent viscosity at 1 sec^{-1} may desirably be in a range of 1 to 5000 poises (p, 20°C).

The ultraviolet ray-curable resin composition of this invention may include an acrylate-type radical curable monomer, an oligomer and a radical curable initiator for the purpose of increasing curability in an early period. The amount of the acrylate-type radical curable monomer and the oligomer to be compounded may desirably be not larger than 20 parts by weight, especially not larger than 15 parts by weight per 100 parts by weight of the resin composition of this invention. The acrylate-type monomer and the oligomer may be known monomers and oligomers, but acryloyl morpholine and urethane acrylate are not preferred because they cause curing obstruction of the resin composition of this invention. The radical curable initiator may be a known one, but alpha-aminoalkylphenone-type photopolymerization initiators are not preferred because these compounds cause curing obstruction of the resin composition of this invention.

Known resins not having a crosslinkable functional group (such as an epoxy group, a hydroxyl group, an oxetanyl group and an unsaturated vinyl group) may be compounded

in the ultraviolet ray-curable resin composition of this invention to alleviate curing shrinkage due to the crosslinkage of the resin or to adjust the hardness of a coated film. Examples of the resins may include acrylic resins and petroleum resins, not limited these resins.

It is possible to mix other known photo-cationic-curing catalysts with the resin composition of this invention. Examples of the other photo-cationic-curing catalysts are preferably triaryl sulfonium salts containing phosphorus as a counter ion from a sanitary characteristic. Preferably specific examples are diphenyl-4-phenylthiophenylsulfonium hexafluorophosphate and bis-[4-(diphenylsulfonio)phenyl] sulfidebis hexafluorophosphate.

[Packaging Container and Container Closure]

A container provided with a coating layer or a printing ink layer may be any packaging container or container closure formed from a metal, a plastic or a laminated body thereof, such as a can or a closure composed of a metal material or a coated metal material, a bottle composed of a thermoplastic resin, and a cup, pouch or tube composed of a laminated body of a thermoplastic resin or a thermoplastic resin metal foil laminated body. In particular, the present invention is useful as an undercoat for a canning can or a cup for heat sterilization such as retort sterilization or for a bottle, a pouch or a tube. The present invention is also useful as a printing ink or a top coating layer. These examples will be described below.

(1) Canning Can and a Container Closure

As the canning can, examples are seamless or press-formed cans formed by draw formation and deep draw formation or draw formation and ironing of a metal material or a resin coated metal material. A thermoplastic resin film such as a polyester is laminated on the surface of a metal substrate, and the laminated body is subjected to a deep draw formation or draw formation and ironing to form a product having excellent corrosion resistance and processability. This polyester coated layer has excellent barrier resistance against mechanical properties and a corrosive component, but has is poor intimate adhesiveness to a white coat, a printing ink, or a finishing varnish. When the resulting can body after providing a coat, an ink or a varnish is subjected to a neck-in processing or a bead processing, there is a problem that the ink or varnish easily peels off.

When the resin composition of this invention is placed on the polyester-coated layer of the can in the form of a white coat or ink, and is subjected to an ultraviolet ray curing, the resin composition did not receive an injury such as peeling even after the resin composition was subjected to a severe neck-in processing or a bead processing. When the contents were filled and after sealing, were subjected to a sterilization by retorting, excellent intimate adhesiveness was maintained and a merchandize value could be increased.

Various surface-treated steel sheets or light metal sheets such as aluminium may be used as a metal sheet constituting the can. As the surface-treated steel sheets, a cold rolled steel sheet is annealed, is secondarily cold rolled, is subjected to at least one surface treatment such as zinc plating, tin plating, nickel plating, and is treated with an electrolytic chromic acid, or with chromic acid. One example of a preferred surface-treated steel sheet is an electrolytically chromic acid-treated steel sheet, especially having 10 to 200 mg/m^2 of a metal chromium layer and 1 to 50 mg/m^2 (calculated as metal chromium) of a chromium oxide layer. This treated steel sheet has an excellent combination of film intimate adhesiveness and corrosion resistance. Another example of the surface-treated steel sheet is a hard tin plate

having 0.5 to 11.2 g/m² of the tin plated amount. This tin plate is desirably subjected to a chromic acid treatment or a chromic acid/phosphoric acid treatment so that the amount of chromium may be 1 to 30 mg/m² calculated as metal chromium. Yet another example is an aluminum-coated steel sheet plated with aluminum, or press-contacted with aluminum. Among these examples, when the above-mentioned technology is applied to the electrolytic chrome treated steel sheet, the effect is especially great.

As the light metal sheet, a pure aluminum sheet and another aluminum alloy sheet may be used. An aluminum alloy sheet having excellent corrosion resistance and processability has a composition comprising 0.2 to 1.5% by weight of Mn, 0.8 to 5% by weight of Mg, 0.25 to 0.3% by weight of Zn, 0.15 to 0.25% by weight of Cu and the remainder containing Al. It is desirable that these light metal sheets are subjected to a chromic acid treatment or a chromic acid/phosphoric acid treatment so that the amount of chromium, calculated as metallic chromium, may become 20 to 300 mg/m².

The thickness of the blank of the metal sheet, namely the thickness (tB) of a can bottom portion, differs depending upon the type of the metal, the use of the container, or the size of the container. Generally, it has a thickness of 0.10 to 0.50 mm. Among the metal sheets, the surface-treated steel sheet preferably has a thickness of 0.10 to 0.30 mm. Furthermore, the light metal sheet preferably has a thickness of 0.15 to 0.40 mm.

A crystalline thermoplastic resin is preferred as a thermoplastic resin to be coated on the metal sheet. Examples of the above resin include an olefin resin film such as polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-vinyl acetate copolymer, ethylene-acrylic acid ester copolymer and an ionomer; polyesters such as polyethylene terephthalate, polybutylene terephthalate, and ethylene terephthalate/isophthalate copolymer; polyamides such as nylon 6, nylon 6,6, nylon 11 and nylon 12; polyvinyl chloride; and polyvinylidene chloride.

Coating of the thermoplastic resin on the metal sheet can be carried out by a heat-melting method, dry lamination and an extrusion coating method. When adhesiveness (heat-melting property) between the coated resin and the metal sheet is poor, it is possible to interpose a urethane-type adhesive, an epoxy-type adhesive, an acid-modified olefin resin-type adhesive, a copolyamide-type adhesive, and a copolyester-type adhesive.

The thickness of the thermoplastic resin is generally 3 to 50 micron (μm), especially 5 to 40 micron. In the case of heat-melting using a film, the film may be unstretched or stretched.

An especially preferred film may be produced by molding a polyester composed of an ethylene terephthalate as a main unit into a film by a film-forming method such as a T-die method or an inflation film-forming method, biaxially stretching the film successively or simultaneously at a stretching temperature of the film, and heat-setting the stretched film.

As a starting polyester, polyethylene terephthalate can be used under markedly restricted stretching, heat-setting and laminating conditions. It is desirable that the maximum degree of crystallization to which the film can reach is decreased in view of impact resistance or processability. To achieve this end, it is desirable to introduce a copolymer ester unit other than ethylene terephthalate into the polyester. It is especially preferred to use a biaxially stretched film of a copolymerized polyester containing an ethylene tereph-

thalate unit as a main component and containing a small amount of another ester unit and having a melting point of 210 to 252° C. The melting point of homopolyethylene terephthalate is generally 255 to 265° C.

The used copolyester should have a molecular weight sufficient for forming a film. For this purpose, the copolyester desirably have an intrinsic viscosity (I. V.) of 0.55 to 1.9 dl/g, especially 0.65 to 1.4 dl/g.

An adhesive primer provided as desired between the polyester film and the metal blank shows an excellent adhesiveness to both of the film and the metal blank. Typical examples of the primer paint having excellent intimate adhesiveness and corrosion resistance include phenol epoxy type paints composed of resol-type phenol aldehyde resins derived from various phenols and formaldehyde, and bisphenol-type epoxy resin, especially paints composed of phenol resins and epoxy resins in a weight ratio of 50:50 to 5:95, especially in a weight ratio of 40:60 to 10:90.

The adhesive primer layer may be provided in a thickness of 0.3 to 5 micron. The adhesive primer layer may be provided on a metal blank or on a polyester film in advance.

Molding into a metal cup container may be carried out by any known means so that the side wall portion may be reduced in thickness. For example, it is carried out by a draw-redraw-ironing processing, a draw-bending-redraw forming and a draw-bending-ironing processing.

For example, according to a deep draw-bending molding (draw-bending-redraw molding), a pre-drawn cup molded from the coated metal sheet is held by an annular holding member inserted in the cup and a redraw die positioned below the above holding member. Coaxially with the holding member and the redraw die, the redraw is arranged so that it can go into and out of the holding member. The redraw punch and the redraw die are relatively moved so that they bite with each other.

The side wall portion of the pre-drawn cup starts from the outer peripheral surface of the annular holding member, passes through a portion defined by the annular bottom surface of the annular holding member bent diametrically and perpendicularly and the upper surface of the redraw die via a curvature corner portion, is bent perpendicularly in an axial direction by the acting corner portion of the redraw die, and can be molded into a deep drawn cup having a smaller diameter than the pre-drawn cup.

The radius of curvature (Rd) of the acting corner portion of the redraw die is adjusted to 1 to 2.9 times, especially 1.5 to 2.9 times, the thickness of a metal sheet blank (tB), whereby thickness reduction can be effectively carried out by the bending and pulling of the side wall portion. In addition, variations in thickness between a lower portion and an upper portion of the side wall portion are dissolved, and uniform thickness reduction becomes possible on the whole. Generally, the side wall portion can be thickness-reduced so that a thickness-reduction rate (R) defined by the following formula is adjusted to 5 to 45%, especially 5 to 40%.

$$R = \frac{tB - tW}{tB} \times 100$$

wherein tB is the thickness of the blank, and tW is the thickness of of the side wall portion.

In the case of a deep drawn can, the draw ratio (RD) defined by the following formula is 1.1 to 3.0 in a first step, and 1.5 to 5.0 as a total.

$$RD = \frac{D}{d}$$

wherein D is the diameter of a laminate material, and d is the diameter of a punch.

An ironing die is provided rearwardly of redraw processing or bending-redraw processing, and the side wall portion can be thickness-reduced so that the thickness-reduction rate including ironing processing becomes 5 to 70%, especially 10 to 60%.

(2) Plastic Packaging Containers

Examples of the plastic packaging containers include a bottle, a cup, a tube, a plastic can, a pouch and a cap.

Molding into plastic containers may be carried out by using an extruder and an injection molding machine. As the extruder, extruders equipped with any screws may be preferably used. As the dies, a flat die and a ring die may be used. In the molding of films, a T-die method and an inflation film-forming method may be used. By hollow molding of an extruded parison, hollow-molded containers such as bottles, tubes and tanks may be produced.

As the injection molding machines, known molding machines provided with an injection plunger or a screw may be used. The above-mentioned plastics are injected into an injection mold through a nozzle, a sprue and a gate whereby the resin flows into an injection cavity and is cooled and solidified to become a preform for a molding container or a stretch blowing molding.

As the plastics constituting the containers, an olefin resin, a polyester resin, a polyamide resin and a polycarbonate are preferably used.

Examples of the olefin resin include low-, medium- or high-density polyethylene (LDPE, MDPE, HDPE), isotactic polypropylene (PP), linear low-density polyethylene (LLDPE), ethylene-propylene copolymer, polybutene-1, ethylene-butene-1 copolymer, propylene-butene-1 copolymer, ethylene-propylene-butene-1 copolymer, ethylene-vinyl acetate copolymer, ionically crosslinked olefin copolymers (ionomers), ethylene-acrylic acid ester copolymer, and blends of these polymers. It is the advantage of this invention that coatings or printing can be applied to resins having a low melting point such as linear low-density polyethylene.

Examples of the polyester include polyesters such as polyethylene terephthalate (PET), polybutylene terephthalate, polyethylene naphthalate and ethylene terephthalate/isophthalate copolymer and blends of such resins.

On the other hand, examples of the polyamide include nylon 6 (N6), nylon 6,6 (N6,6), nylon 11 and nylon 12; copolyamides such as nylon 6/6,6; and blends of at least two of the above polyamides.

As polycarbonate (PC), polycarbonates from bis phenols such as bisphenol A or F, and polycarbonate Z may be used.

Plastic containers or webs for forming pouches may be a single layer plastic container or web, or a multilayer plastic container or web. For example, they may be a laminate composed of the same resins composed of a linear low-density polyethylene as an outside surface layer and a high-density polyethylene or isotactic polypropylene as an inner layer, or a laminate composed of different types of resins such as an olefin resin and a polyester or a polyamide. Of course, the above molded article or web is not limited to a two layer combination, and it may be composed of multilayers or three or four layers or more.

These plastic containers or webs may include other plastics or metal foils. For example, to impart gas impermeabil-

ity to oxygen to containers formed, a gas barrier resin or an aluminum foil or a steel foil may be assembled in a multi-layer structure.

A gas barrier resin may generally have an oxygen permeability coefficient (PO_2) of 5.5×10^{-12} cc.cm/cm².sec.cm Hg or below, especially 4.5×10^{-12} cc.cm/cm².sec.cm Hg or below. The barrier resin may be an ethylene-vinyl alcohol copolymer having an ethylene content of 20 to 50 mole % and an unsaponified vinyl ester residue content of not larger than 5 mole %, and a homopolyamide, a copolyamide or a blend thereof containing 3 to 30, especially 4 to 25, of amide groups per 100 of carbon atoms. Of course, the above-mentioned ethylene-vinyl alcohol copolymer and the polyamide may be used in the form of a blend. Within the range which does not impede the essence of the resin, for example in a range of not larger than 20% by weight of another thermoplastic resin such as a resin for imparting adhesiveness between polyolefins may be used as a blend. These gas barrier resins can be provided as a very thin layer compared with the entire thickness. Even if these resins have absorptions in the near infrared region, their effects are small.

To substitute for the intermediate layer, or together with the above intermediate layer, a resin layer containing an oxygen absorbing agent or a resin layer containing a dryer may be provided as an intermediate layer. Furthermore, to re-use a regrind (scrap resin), it may be used as an intermediate layer.

The coating layer or the printing ink layer may be directly provided on the plastic molding containers. The application of the coating layer or the printing ink layer on the pouch can be carried out on the web before bag making, and thereafter bag making is carried out by heat sealing.

[Application and curing]

Coating of ultraviolet ray-curable paint, such as an undercoat of white coat, est., may be performed by using a gravure roll, or an ordinary coating roll. The coating thickness of white coat is generally in a range of 3 to 20 micron.

On the other hand, the ultraviolet ray-curable ink may be printed by a known can-making printing method such as offset printing, lithography, gravure printing and screen printing.

When two layers of a printing ink layer and a finishing varnish layer are provided, the two layers are formed in a wet-on-wet relation and these are subjected to ultraviolet curing to cure them at a stroke.

When three layers of a white coat layer a printing ink layer and a finishing varnish layer are provided, at first, the white coat layer is formed and cured, and then the printing ink layer and the finishing varnish layer are formed in a wet-on-wet relation and both layers are subjected to ultraviolet curing to cure them at a stroke.

Ultraviolet rays used to cure the ink layer are rays which include a near ultraviolet region and generally have a wavelength of 200 to 440 nm, especially 240 to 420 nm. A halide lamp, a high-pressure mercury lamp, and a low-pressure mercury lamp are used as an ultraviolet light source. Since the thickness of the ink layer or the finishing varnish layer is extremely small, it is an advantage that the energy required for curing may be small. An energy of 500 to 5000 joule/m² is generally sufficient.

The coating layer and the printing ink layer after irradiation of ultraviolet rays, as desired, are heated at a temperature of 30 to 80° C. whereby distortions are removed and post-curing is carried out. Of course, this operation is arbitrary.

15

EXAMPLES

The present invention will be described in detail by the following Examples.

[Production of initiators]

(1) 2-Naphthyl-1-ethoxycarbonylethylmethylsulfonium hexafluorophosphate (catalyst 1)

2-Naphthyl-1-ethoxycarbonylethylsulfide (27.64 g) was mixed with 13.24 g of dimethylsulfuric acid and the mixture was reacted at 80° C. for 10 hours. The reaction product was dissolved in 300 ml of distilled water and 100 ml of ethyl acetate. The solution was stirred, and the aqueous solution layer was taken out, and 18.41 g of potassium hexafluorophosphate and 300 ml of ethyl acetate were added to the aqueous solution layer. The solution was stirred vigorously. The ethyl acetate layer was washed with 100 ml of distilled water two times. The water of the ethyl acetate layer was removed with anhydrous magnesium sulfate. Then, ethyl acetate was evaporated, followed by drying at 40° C. under reduced pressure to give the desired product.

(2) 2-Naphthyl-1-methoxycarbonylethylmethylsulfonium hexafluorophosphate (catalyst 2)

2-Naphthyl-1-methoxycarbonylethylsulfide (24.63 g) was mixed with 13.24 g of dimethylsulfuric acid, and the mixture was reacted at 80° C. for 10 hours. The reaction product was dissolved in 300 ml of distilled water and 100 ml of ethyl acetate. The mixture was stirred, and the aqueous solution layer was taken out. Potassium hexafluorophosphate (18.41 g) and 300 ml of ethyl acetate were added to the aqueous solution layer, and the mixture was vigorously stirred. The ethyl acetate layer was washed twice with 100 ml of distilled water. The water of the ethyl acetate layer was removed with anhydrous magnesium sulfate, and then ethyl acetate was evaporated, followed by drying at 40° C. under reduced pressure to give the desired product.

(3) 2-Naphthyl-1-ethoxycarbonylpropylmethylsulfonium hexafluorophosphate (catalyst 3)

2-Naphthyl-1-ethoxycarbonylpropylsulfide (27.44 g) was mixed with 13.24 g of dimethylsulfuric acid, and the mixture was reacted at 80° C. for 10 hours. The reaction product was dissolved in 300 ml of distilled water and 100 ml of ethyl acetate, the solution was stirred to take out the aqueous solution layer. Potassium hexafluorophosphate (18.41 g) and 300 ml of ethyl acetate were added to the aqueous solution layer, and the mixture was stirred vigorously. The ethyl acetate layer was washed twice with 100 ml of distilled water, the water of the ethyl acetate layer was removed with anhydrous magnesium sulfate, and the ethyl acetate was evaporated, followed by drying at 40° C. under reduced pressure to give the desired product.

[Production of a paint and ink]

In accordance with the composition described in Table 1, an alicyclic epoxy resin, a reactive diluent, an initiator composition and titanium dioxide, etc, were mixed, and fully kneaded by a 3 roll system to prepare a paint and an ink.

[Method of evaluating the properties of a coated film]

(1) Curability: Presence or absence of a tacky feeling through examination by touch.

(2) Transferability: After a packaging container is transferred in an ordinary line, the injury of a coating cured by ultraviolet rays, and the state of peeling were evaluated by seeing with eyes.

(3) Blocking property:

(i) Metal sheet; 1000 coated metal sheets were piled, and after standing for one day at 50° C., the result was evaluated by the ease of peeling of the sheets.

(ii) Film: The printed film was wound up through 1000 m, and after standing for one day at room temperature, the

16

result was evaluated by the ease of peeling at the time of winding off.

(4) Color of a coated portion and a printed portion: Evaluated by seeing with eyes to determine whether the yellowish color was within the acceptable range.

(5) Heat-resistant treatability: A gloss down and a surface roughening of a coated film cured with ultraviolet rays were detected by examination of seeing with eyes when the film was heat-treated in a production step of the container.

(6) Retorting treatment: 125° C.-30 minutes retorting with vapor. In the case of a metal can, whiteness, blister and gloss down of the coated film by retorting were evaluated with eyes. In the case of a pouch, the result was evaluated by the presence or absence of delamination.

Example 1

To both surfaces of a tin-free steel sheet having a blank thickness of 0.18 mm and a tempering degree of DR-9 (as surface treated coated amount, the amount of metallic chrome 120 mg/m², the amount of chromium oxide 15 mg/m²), a biaxially stretched polyethylene terephthalate/isophthalate copolymerized film having a thickness of 20 micron was heat-adhered simultaneously at both surfaces, and immediately cooled with water to form an organic coated metal sheet. The organic coated metal sheet was coated with paraffin wax uniformly, and punched into a circular sheet having a diameter of 160 mm, and molded into a shallow drawn cup in accordance with a customary manner. The draw ratio in this drawing step was 1.59.

The shallow drawn cup was subjected to a primary and secondary redraw formations to obtain a thickness-reduced deep drawn cup. The re-draw formation step molding conditions and the properties of the deep drawn cup by the re-draw formation are shown below.

| | |
|---|---------|
| Primary re-draw ratio | 1.23 |
| Secondary re-draw ratio | 1.24 |
| Radius of curvature of a re-draw die working corner | 0.30 mm |
| Radius of curvature of a re-draw die holding corner | 1.0 mm |
| Cup diameter | 66 mm |
| Cup height | 130 mm |
| Side wall thickness reduction rate | -40% |

Thereafter, the cup was subjected to a dome molding by a fixed method, and the deep drawn cup was heat-treated at 215° C. for 1 minute to remove processing distortions of the film and evaporate the lubricant. Then, the edge of the opening end portion was cut off to give a thickness-reduced deep-drawn can having a height of 123 mm.

This thickness-reduced deep-drawn can was coated with Paint A to give a film thickness of 10 micron, and the film was cured by irradiating ultraviolet rays having 500 mJ/cm² (using a photometer corresponding to a gallium lamp) with the gallium lamp having an output of 240 W/cm. The amount of titanium dioxide contained in the white coated film was 0.67 mg/cm² per unit area of the coated film. The cured coated film did not have a tack, nor had a problem in color such as strong yellowish color. Then, to print on a white-coated can, the can was transferred through an ordinary line from the coater to the printer. The injury or peeling of the white coated film due to contact with the guide and contact with the can to the can was not seen. According to a customary procedure, a heat-curable ink and a thermoset-

17

ting finishing varnish were printed and baked on the can, and further the can was subjected to a neck-in molding. Then, the can was packed with water, and a closure was seamed and was subjected to retorting treatment. The can had good retorting resistance.

Example 2

The can was evaluated in the same way as in Example 1 except that Paint B was coated so that the thickness of the coated film had 6 micron. In the same way as in Example 1, the coated film had good curability, color, transferability, heat-resistant treatment and retorting resistance. In this case, the amount of titanium dioxide contained in the white coated film was 0.40 mg/cm² per unit area of the coated film.

Example 3

The can was evaluated in the same way as in Example 1 except that Paint C was coated. In the same way as in Example 1, the coated film had good curability, color, transferability, heat-resistant treatment and retorting resistance. In this case, the amount of titanium dioxide contained in the white coated film was 0.67 mg/cm² per unit area of the coated film.

Example 4

The can was evaluated in the same way as in Example 1 except that Paint D was coated. In the same way as in Example 1, the coated film had good curability, color, transferability, heat-resistant treatment and retorting resistance. In this case, the amount of titanium dioxide contained in the white coated film was 0.67 mg/cm² per unit area of the coated film.

Comparative Example 1

The can was evaluated in the same way as in Example 1 except that Paint F was coated. Since the amount of the photo-cationic-curing resin was lower than the range of this invention and was less than 1% by weight based on titanium dioxide, sufficient curability could not be obtained. The cured coated film was in an almost uncured state.

Comparative Example 2

The can was evaluated in the same way as in Example 1 except that Paint G was coated. Since the amount of the photo-cationic-curing catalyst exceeds the range of the invention, there was no problem with respect to curability and transferability. In baking after the printing, surface roughening was recognized. However, gloss down, whitening and blister due to retorting did not occur.

Comparative Example 3

The can was evaluated in the same way as in Example 1 except that Paint H was coated. Since the amount of the sensitizer was lower than the range of this invention and was less than 1% by weight based on titanium dioxide, sufficient curing could not be obtained, and the cured coated film had a tack. The injury or peeling of the coated film was marked by contacting between cans during transferability in the printing step. In the baking after the printing, gloss down occurred. However, by the effect of the thermosetting property of the photo-cationic-curing catalyst, there was no occurrence of gloss down, whitening and blister due to retorting.

Comparative Example 4

The can was evaluated in the same way as in Example 1 except that Paint I was used. Since the amount of the

18

sensitizer exceeded the range of this invention and was larger than 5% by weight based on titanium dioxide, the white coated film was yellowish and had a very poor outside appearance.

Comparative Example 5

The can was evaluated in the same way as in Example 1 except that Paint K was coated. Since the amount of the sensitizer exceeded the range of this invention and was larger than 5% by weight based on titanium dioxide, the white coated film was yellowish and had a very poor outside appearance.

Example 5

A tinplate having a blank thickness of 0.245 mm, a temper degree of 4 and a specification of E 2.8/2.8 was punched into a circular plate having a diameter of 142 mm, and the circular tinplate was molded into a cup at a draw ratio of 1.6 and was subjected to steps of re-draw formation (draw ratio of 1.3) and ironing molding (3 steps, a total reduction 67%), and molded into a drawn and ironed cup having an inside diameter of 66 mm. This drawn and ironed cup was cut at the edge of an opening end portion so that its height became 123 mm. By a customary manner, the cup was washed, treated and dried to obtain a drawn-ironed can.

This drawn-ironed can was coated with Paint E to form a film having 8 micron, and the coated film was cured by irradiating ultraviolet rays of 500 mJ/cm² (using a photometer corresponding to a gallium lamp) by using the gallium lamp having an output of 240 W/cm. The amount of titanium dioxide contained in the white coated film was 0.54 mg/cm² per unit area of the coated film. The cured film did not have a tack, and there was no problem in color such as a strong yellowish shade. Thereafter, to print the white coated can, the can was transferred through an ordinary line from the coater to the printer, but the injury or peeling of the white coated film due to the contact with the guide or cans with each other was not seen. According to a customary method, the can was printed and baked by using a thermosetting ink and a heat-setting finishing varnish, and then the inner surface of the printed can was sprayed and again baked. When the baked outside surface of the can was compared with the state before baking, no problem such as gloss down due to the lack of curing of the white coated film was seen. Thereafter, this can was subjected to a neck-in molding, and the can was packed with sodium bicarbonate and water, and a closure was seamed on the can and the can was retorted. The can had good retorting resistance.

Example 6

Both surfaces of a tin-free steel sheet having a blank thickness of 0.22 mm and a tempering degree of T4CA and having a vertical size of about 1 m and a width of about 1 m (as a surface-coated amount, the amount of metallic chrome of 120 mg/m² and the amount of chromium oxide of 15 mg/m²) were coated with an epoxyphenol-type thermosetting paint, and the coated film was baked. Then, the outside surface of the can of the coated sheet was coated with Paint A with a film thickness of 10 micron, and the coated film was cured by irradiating ultraviolet rays having 500 mJ/cm² (using a photometer corresponding to a gallium lamp) with the gallium lamp having an output of 240 W/cm. The amount of titanium dioxide contained in the white coated film was 0.67 mg/cm² per unit area of the coated film. With respect to the cured coated film did not have a problem of a tack, yellowishness, and blocking. Furthermore, print-

ing was carried out on the white coated film by a sheet-fed press using a thermosetting ink and a heat-curable finishing varnish, but there was no injury or peeling on the white coated film on an outside surface due to the transferring of the sheet. Furthermore, no gloss down was seen due to baking. Then, the printed sheet was cut by a customary method, and by using a nylon-type adhesive, a can body for a cylindrical adhesion can was formed. Furthermore, neck-in molding was carried out at both ends of the cylinder, and a bottom closure was sealed to a side which would become a bottom portion. Thereafter, the bottom-equipped adhesion can was packed with water, and a top closure was sealed to perform retorting treatment. The retorting resistance was good.

Comparative Example 6

The sheet and the can were evaluated in the same way as in Example 6 except that Paint J was coated. Since the amount of the sensitizer was lower than the range of this invention and was less than 1% by weight based on titanium dioxide, sufficient curing could not be obtained, and the coated sheet caused blocking and had much injury or peeling during transfer. Furthermore, gloss down occurred during baking after the printing. However, there was no gloss down, whitening and blister due to retorting by the effect of the thermosetting property of the photo-cationic-curing catalyst.

Example 7

High-density polyethylene pellets were inserted in an extruder, melted and kneaded, and then, a pipe-shaped product (called "parison") having a diameter of 20 mm was prepared within a die head at the end of the extruder. This parison was inserted in a split mold, a parison portion corresponding to the bottom portion was melted, air was blown, and the melted parison portion was cooled and solidified in the mold and taken out from the mold. An unnecessary burr was removed to give a mouth-containing cylindrical plastic bottle. The outside surface of this bottle was frame-treated, and an ink A as printed to form a coating thickness of 18 micron, and the coated film was cured by irradiating ultraviolet rays having 500 mJ/cm² (using a photometer corresponding to a gallium lamp) with the gallium lamp having an output of 240 W/cm. In this case, the

amount of titanium dioxide contained in the white coated film was 0.79 mg/cm² per unit area of the coated film. The cured film had no tack, nor had a problem of color such as strong yellowishness. The plastic bottle after printing was put into an exclusive carton of corrugated board, and a transportation test was carried out using a truck. However, no injury or peeling of the inked coated film was noted. The bottle showed a good quality.

Example 8

Ink B was printed to a biaxially stretched polyethylene terephthalate film having a thickness of 12 micron corona treated on a side of a printed surface so that a film thickness of 5 micron was obtained. The coated film was cured by irradiating ultraviolet rays having 200 mJ/cm² (using a photometer corresponding to a gallium lamp) with the gallium lamp having an output of 240 W/cm. In this case, the amount of titanium dioxide contained in the white coated film was 0.43 mg/cm² per unit area of the coated film. The cured film had no tack, nor a problem of color such as a strong yellowishness. The blocking property of the film was evaluated, but there was no particular problem. The film was pasted with an aluminum foil having a thickness of 7 micron by using a urethane-type adhesive so that the side of the printed surface of the printed film would become an aluminum foil side. On the other surface of this aluminum foil, a polypropylene film having a thickness of 50 micron was pasted with an ordinary method as an inner surface material of the container. The prepared three-layer laminated body was cut, and by heat-sealing, a bag having an opening end only on one side was prepared. This bag was packed with water, the opening end is heat-sealed, and the bag was treated by retorting. A problem of delamination due to the curing insufficiency of the ink was not at all recognized, and good retorting resistance was shown.

Table 2 shows the evaluation results mentioned in Examples and Comparative Examples. The results are expressed by the following items.

- : good
- △: slightly bad
- X: bad
- : not evaluated

TABLE 1

| Components | Coating composition | | | | | | | | | | | Ink composition | |
|--|---------------------|------|------|------|------|------|------|------|------|------|------|-----------------|----|
| | A | B | C | D | E | F | G | H | I | J | K | A | B |
| (1) 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 45 | 50 |
| (2) limonen dioxide | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | | |
| (3) bisphenol F-type epoxy resin (epoxy equivalent 4300) | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | | |
| (4) hydroxybutylvinylether | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | | |
| (5) hexanediolmonovinylether | | | | | | | | | | | | 5 | |
| (6) epoxidized polybutadiene | | | | | | | | | | | | 10 | |
| (7) catalyst 1 | 2 | | | 2 | 1 | 0.3 | 10 | 2 | 2 | 2 | 2 | 3 | 2 |
| (8) catalyst 2 | | 2 | | | | | | | | | | | |
| (9) catalyst 3 | | | 2 | | | | | | | | | | |
| (10) 2,4-diethylthioxanthone | 1 | 0.6 | 1 | | 1.5 | 2 | 1 | 0.3 | 3 | | | | 1 |
| (11) isopropyl thioxanthone (2,4-isomeric mixture) | | | | 2 | | | | | | 0.3 | 3 | 1 | |
| (12) silicone resin | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | | |
| (13) polyethylene wax | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | |

TABLE 1-continued

| Components | Coating composition | | | | | | | | | | | Ink composition | |
|-----------------------------------|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----------------|-----|
| | A | B | C | D | E | F | G | H | I | J | K | A | B |
| (14) lanoline wax | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| (15) dispersing agent | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| (16) rutile-type titanium dioxide | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 30 | 50 |
| (17) silica fine powder | | | | | | | | | | | | 10 | |

TABLE 2

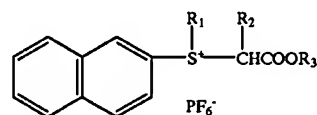
| Examples and Comp. | Paints and inks applied | Containers applied | Amount of titanium dioxide per unit area of the coated film (mg/cm ²) | Weight % of photo-cationic-curing catalyst when the weight of titanium dioxide was 100% | Weight % of sensitizer when the weight of titanium dioxide was 100% | Results of evaluation | | | | | |
|--------------------|-------------------------|----------------------------------|---|---|---|-----------------------|----------------------------|------------------|--|------------------------------|----------------------|
| | | | | | | Cur-ability | Color of the UV-cured film | Trans-ferability | Blocking resistance | Heat-resistant treat-ability | Retorting resistance |
| Ex.1 | paint A | Thickness-reduced deep drawn can | 0.67 | 5 | 2.5 | ○ | ○ | ○ | — | ○ | ○ |
| Ex.2 | paint B | Thickness-reduced deep drawn can | 0.40 | 5 | 1.5 | ○ | ○ | ○ | — | ○ | |
| Ex.3 | paint C | Thickness-reduced deep drawn can | 0.67 | 5 | 2.5 | ○ | ○ | ○ | — | ○ | |
| Ex.4 | paint D | Thickness-reduced deep drawn can | 0.67 | 5 | 5 | ○ | ○ | ○ | — | ○ | |
| Ex.5 | paint E | Drawn and ironed can | 0.54 | 2.5 | 3.75 | ○ | ○ | ○ | — | ○ | |
| Ex.6 | paint A | Adhesion can (3-piece can) | 0.67 | 5 | 2.5 | ○ | ○ | ○ | ○ | ○ | |
| Ex.7 | ink A | Plastic bottle | 0.79 | 10 | 3.3 | ○ | ○ | ○ | — | — | — |
| Ex.8 | ink B | Pouch | 0.43 | 4 | 2 | ○ | ○ | ○ | ○ | — | ○ |
| Comp.Ex1 | paint F | Thickness-reduced deep drawn can | 0.67 | 0.75 | 5 | X | ○ | | Evaluation impossible because of poor curability | | |
| Comp.Ex2 | paint G | Thickness-reduced deep drawn can | 0.67 | 25 | 2.5 | ○ | ○ | ○ | — | Δ | ○ |
| Comp.Ex3 | paint H | Thickness-reduced deep drawn can | 0.67 | 5 | 0.75 | Δ | ○ | X | — | X | ○ |
| Comp.Ex4 | paint I | Thickness-reduced deep drawn can | 0.67 | 5 | 7.5 | ○ | X strong yellowness | ○ | — | ○ | ○ |
| Comp.Ex5 | paint K | Thickness-reduced deep drawn can | 0.67 | 5 | 7.5 | ○ | X strong yellowness | ○ | — | ○ | ○ |
| Comp.Ex6 | paint J | Adhesion can (3-piece can) | 0.67 | 5 | 0.75 | Δ | ○ | X | X | X | ○ |

55

What is claimed is:

1. A packaging container having, on the outer surface, a coating layer of a resin composition which comprises

60



(A) a cationic curable resin comprising an alicyclic epoxy resin,

65

(B) a photo-cationic-curing catalyst comprising a compound of the following formula (1),

wherein each of R₁ and R₂ is an alkyl group, and they may be the same or different, and R₃ is an alkyl group, (C) a sensitizer comprising a thioxanthone sensitizer, and (D) a pigment comprising titanium dioxide,

23

said resin composition being cured by ultraviolet ray, wherein

the amount of said titanium dioxide is at least 0.30 mg per 1 cm² of said coating layer,

the amount of said photo-cationic-curing catalyst is 1 to 20% by weight with regards to said titanium dioxide, and

the amount of said sensitizer is 1.5 to 5% by weight with regards to said titanium dioxide.

2. A packaging container according to claim 1, wherein the photo-cationic-curing catalyst is 2-naphthyl-1-ethoxycarbonylethylmethylsulfonium hexafluorophosphonate, 2-naphthyl-1-methoxycarbonylethylmethylsulfonium hexafluorophosphonate, or 2-naphthyl-1-ethoxycarbonylpropylmethylsulfonium hexafluorophosphonate.

3. A packaging container according to claim 1 or 2, wherein the container is a can composed of a metallic material.

4. A packaging container according to claim 1 or 2, wherein the container is a bottle composed of a thermoplastic resin.

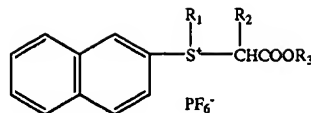
5. A packaging container according to claim 1 or 2, wherein the container is a pouch composed of a thermoplastic resin laminate or a thermoplastic resin-metal foil laminate.

6. A container closure having, on the outer surface, a coating layer of a resin composition which comprises

(A) a cationic curable resin comprising an alicyclic epoxy resin,

(B) a photo-cationic-curing catalyst comprising a compound of the following formula (1),

24



wherein each of R₁ and R₂ is an alkyl group, and they may be the same or different, and R₃ is an alkyl group, (C) a sensitizer comprising thioxanthone sensitizer, and (D) a pigment comprising titanium dioxide, said resin composition being cured by ultraviolet ray, wherein

the amount of said titanium dioxide is at least 0.30 mg per 1 cm² of said coating layer,

the amount of said photo-cationic-curing catalyst is 1 to 20% by weight with regards to said titanium dioxide, and

the amount of said sensitizer is 1.5 to 5% by weight with regards to said titanium dioxide.

7. A container closure according to claim 6, wherein the photo-cationic-curing catalyst is 2-naphthyl-1-ethoxycarbonylethylmethylsulfonium hexafluorophosphonate, 2-naphthyl-1-methoxycarbonylethylmethylsulfonium hexafluorophosphonate, or 2-naphthyl-1-ethoxycarbonylpropylmethylsulfonium hexafluorophosphonate.

8. A container closure according to claim 6 or 7, wherein the container closure is a closure composed of a metallic material.

9. A container closure according to claim 6 or 7, wherein the container closure is a closure composed of a thermoplastic resin.

* * * * *

United States Patent [19]

Bauer et al.

[11] Patent Number: **5,077,174**

[45] Date of Patent: **Dec. 31, 1991**

[54] **POSITIVE WORKING DRY FILM ELEMENT
HAVING A LAYER OF RESIST
COMPOSITION**

[75] Inventors: **Richard D. Bauer**, Kennett Square,
Pa.; **Gwendyline Y. Chen**,
Wilmington, Del.; **Walter R. Hertler**,
Kennett Square, Pa.; **Robert C.**
Wheland, Wilmington, Del.

[73] Assignee: **E. I. Du Pont de Nemours and
Company**, Wilmington, Del.

[21] Appl. No.: **507,337**

[22] Filed: **Apr. 10, 1990**

[51] Int. Cl.⁵ **G03C 1/76**

[52] U.S. Cl. **430/270; 430/271;
430/326; 522/31; 522/127; 522/154**

[58] Field of Search **430/220, 326, 271;
522/31, 127, 154**

[56] References Cited

U.S. PATENT DOCUMENTS

| | | | |
|-----------|--------|------------------|---------|
| 4,316,046 | 4/1982 | Dossell | 430/270 |
| 4,678,737 | 7/1987 | Schneller et al. | 430/270 |
| 4,898,803 | 2/1990 | Aoi et al. | 430/270 |
| 4,951,379 | 6/1990 | Brunsvold et al. | 430/270 |

Primary Examiner—**Jack P. Brammer**

[57] ABSTRACT

This invention relates to positive working resist compositions having utility in dry film photoresists and to fully aqueous methods for developing and stripping them.

27 Claims, No Drawings

POSITIVE WORKING DRY FILM ELEMENT HAVING A LAYER OF RESIST COMPOSITION

FIELD OF THE INVENTION

This invention relates to positive working resist compositions having utility in dry film photoresists and to fully aqueous processes for developing and stripping them.

BACKGROUND OF THE INVENTION

Modern high resolution photoresists require high photospeed for productivity, superior image integrity, and fully aqueous development and stripping. All aqueous processing is needed because the organic solvents that have been used in the past are being replaced because of increasingly demanding environmental restrictions.

In U.S. Pat. No. 3,779,778, novel photosolubilizable compositions are disclosed that comprise 1) a water-insoluble compound containing one or more acid-degradable groups, and 2), a photoinitiator comprising a photolizable acid progenitor. The useful water-insoluble compounds can contain one or more acid-degradable linkage which can be formed by the nucleophilic reaction of phenols, N-alkyl arylsulfonamides, or certain secondary amines with alkyl vinyl ethers, e.g. methyl vinyl ether, ethyl vinyl ether or a dihydropyran.

A dry film resist prepared according to this invention from the tetrahydropyranyl ether of a phenolic resin and a photoacid generator required a mixture of a flammable organic alcohol, potassium hydroxide and water to develop away the exposed areas.

European Patent Application 0 264 908 discloses resists comprised of at least one polymer, copolymer, or terpolymer having recurrent acid labile groups pendant to the polymer backbone wherein the improvement comprises: selecting a substituent side chain on said acid labile groups which is capable of forming secondary carbonium ion intermediates and having an available proton adjacent to the carbonium ion formed during cleavage. The autodecomposition temperature of the polymer comprising the photoresist is increased, to a temperature greater than about 160° C., by selecting substituent side chains on the acid labile group which exhibit a less stable intermediate carbonium ion than the t-butyl ion.

In U.S. Pat. No. 4,491,628, resists sensitive to UV, electron beam and x-ray radiation with positive or negative tone upon proper choice of a developer are formulated from a polymer having recurrent pendant groups such as tert-butyl ester or tert-butyl carbonate groups that undergo efficient acidolysis with concomitant changes in polarity (solubility) together with a photoinitiator which generates acid upon radiolysis. A sensitizer component that alters wavelength sensitivity of the composition may also be added. The preferred acid labile pendant groups are tert-butyl esters of carboxylic acids and tert-butyl carbonates of phenols but, it is understood that a wide range of acid labile groups are operative in the invention. These include trityl, benzyl, benzhydryl modifications as well as others well known in the art.

A dry film resist prepared according to this invention from poly(tert-butyl acrylate) and a photoacid generator required heating of the exposed image at 100° C. for up to 15 minutes in order to solubilize the polymer in

fully aqueous base. The resulting developed image had ragged edges.

The production of printed circuits using a variety of resists is described in "Printed Circuits Handbook" edited by Clyde F. Coombs, Second Edition, published by McGraw-Hill, Inc., 1979. Chapter 6 of this publication describes the use of both negative-working and positive-working photoresists in the preparation of printed circuits. In particular, section 14 of this chapter discusses conventional positive-working liquid photoresists and section 16 discusses conventional coating methods for applying such photoresists to printed circuit substrates. Likewise, the production of printed circuits using photoresists is described in "Photoresist Materials and Processes" by W. S. DeForest published by McGraw-Hill Book Company, 1975. In particular, Chapter 5 of this publication discusses conventional positive resists and the processes of their use to manufacture printed circuits.

U.S. Pat. No. 3,469,982 discloses a process for forming a photoresist comprising (1) applying to a surface the surface of a solid unexposed photosensitive layer of thermoplastic photohardenable material, the other surface being adhered to a film support, then in either order (2) exposing the layer, and (3) stripping the support, and then (4) washing away the unexposed areas of the layer. The surface bearing the resist can be etched, plated, or treated in other ways. The photoactive materials disclosed in this case are photopolymerizable compounds.

Typical fully aqueous negative acting dry film photoresists used in the process described in this invention are described in Gilano, U.S. Pat. No. 3,887,450. They contain alkali soluble carboxylic acid containing polymers and photocrosslinkable acrylic acid monomers. Such compositions are developable in aqueous alkali and strippable in stronger aqueous alkali. However, they have marginal resistance, if any, to alkaline processes such as ammoniacal cupric chloride etchants or electrodeless copper plating baths which are typically used to form copper circuits. These negative acting coatings cannot be imagewise re-exposed with the same radiation used to produce the original image and developed to form a second image which could be used to modify the substrate a second time.

A very useful property of negative acting dry film photoresists is the capacity to cover or "tent" over holes in the substrate which need to be protected from the reagents which are used to modify the substrate. For example, if there are plated holes in the substrate that will ultimately provide electrical contact between circuit traces on both sides of the circuit panel, they must be protected during an etching operation that would be used to form the circuit traces. The tents often require a high level of exposure to crosslink them sufficiently so that they are not attacked by the alkaline development process; that level of exposure is often too high for optimum artwork reproduction.

U.S. Pat. No. 4,193,797 discloses a positive active dry film process for forming a photoresist comprising (1) applying to a surface the surface of a solid unexposed photosensitive layer of thermoplastic photosoluble or photodensitizable material, the other surface being releasably adhered to a film support, then in either order (2) exposing the layer to actinic radiation, and (3) removing the film support, and then (4) washing away exposed areas of the layer to uncover areas of the underlying surface. The uncovered areas of the underlying

3

ing surface can be etched, plated or otherwise modified. The photoactive materials disclosed in this invention include photodesensitizable bisdiazonium salt compositions, which required solvent development, and photosolubilizable o-quinone-diazides. These suffer from inherently high optical density in anything but thin coatings and slow photospeed. The thin coatings described in this invention (0.35 mils) would hardly be useful in typical dry film resist processes like plating and tenting.

The positive acting dry film resist compositions of the current invention are fully aqueous, have high photospeed, do not require the use of high temperature bakes after exposure to solubilize the exposed image, can tent over holes in the substrate, and give high resolution images with good line quality. Properly formulated, the resist image can withstand both alkaline and acid etching and plating processes typically used to modify substrates in the preparation of printed circuit boards. The resist image can then be blank exposed and stripped in aqueous alkali or re-exposed imagewise and developed so that the substrate can be modified a second time without the need to apply a second resist.

The resist compositions of the instant invention contain thermally stable but acid labile α -alkoxyalkyl esters of carboxylic acids, e.g., tetrahydropyranyl esters.

J. E. Kearns et al., J. Macromol. Sci.-Chem. A8(4), pp. 673-685 (1974) describe the preparation and deesterification of a number of polymers and copolymers of unsaturated tetrahydropyranyl esters. The utility of dihydropyran as a protecting group in the preparation of polymers containing other groups susceptible to normal hydrolysis conditions is ascribed to the mild conditions required to remove the tetrahydropyranyl group from these esters.

None of the prior art of which we are aware shows the use of the polymers of the present invention in dry film photoresist compositions. Moreover, none of the prior art of which we are aware discloses resist formulations usable in dry film photoresists containing a polymer bearing recurring pendant acid labile groups that possess the structures disclosed in the present invention.

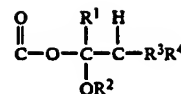
SUMMARY OF THE INVENTION

The present invention lies in resist formulations capable of being used in dry film photoresist applications that contain polymers that possess recurring pendant acid labile α -alkoxy alkyl carboxylic acid ester groups in the presence of an acid generator activated by incident radiant energy.

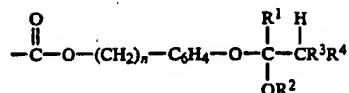
The present invention provides a dry film photoresist element capable of developing a latent image without post exposure elevated temperature and developable to a resist image in an all aqueous alkali comprising a thin flexible polymeric film support having adhered thereto with low to moderate adherence a solid photosensitive layer having a thickness of about 0.3 mils (~8 microns) or greater said layer comprising:

- (a) a polymer chosen from the group consisting of compositions having a polymer backbone and pendant acid-labile groups which are bound directly or indirectly to the polymer backbone, said pendant acidlabile groups represented by the formula:

4



or



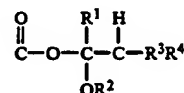
where R¹ is hydrogen or lower alkyl (up to about 6 carbon atoms); R² is lower alkyl (up to about 6 carbon atoms); and R³ and R⁴ independently are hydrogen or lower alkyl where the definition of lower alkyl includes the joining of R¹ and R² or R¹ and either R³ or R⁴, or R² and either R³ or R⁴ to form a 5-, 6-, or 7-membered ring;

- (b) an initiator system comprising an initiator or an initiator and at least one sensitizer, that forms upon exposure to actinic radiation having a wavelength between about 3000Å and about 9000Å, a catalytic amount of a strong acid preferably having a pKa equal to or less than 2; and

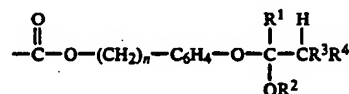
- (c) optionally additives such as, but not limited to, plasticizers, colorants, adhesion promoters and surfactants.

The present invention also provides a process for forming a positive photoresist on a surface which comprises:

- a. applying to said surface the surface of a solid, unexposed, photosensitive layer having a thickness of at least 0.3 mils (~8 microns), said layer comprised of (a) a polymer chosen from the group consisting of compositions having a polymer backbone and pendant acid-labile groups which are bound directly or indirectly to the polymer backbone, said pendant acidlabile groups represented by the formula:



or



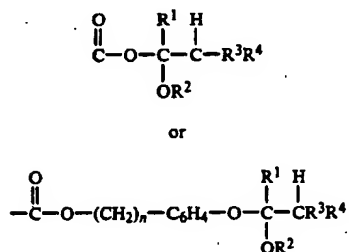
where n=0-4; R¹ is hydrogen or lower alkyl (up to about 6 carbon atoms); R² is lower alkyl (up to about 6 carbon atoms); and R³ and R⁴ independently are hydrogen or lower alkyl where the definition of lower alkyl includes the joining of R¹ and R² or R¹ and either R³ or R⁴, or R² and either R³ or R⁴ to form a 5-, 6-, or 7-membered ring; (b) an initiator system that forms a catalytic amount of strong acid upon exposure to actinic radiation having a wavelength between about 3000Å and about 9000Å; and (c) optionally, plasticizers, colorants and adhesion promoters, surfactants, the other surface of the layer having adhered thereto with low to moderate adherence a thin, flexible, polymeric film support; then in either order;

5

- b. exposing the layer, imagewise, to actinic form an image;
- c. stripping the film support from the resulting image-bearing layer; and then;
- d. washing away the exposed areas of the layer to form a positive resist image;
- e. permanently modifying the adjacent areas on the substrate surface which are unprotected by the resist image by using a reagent capable of etching said areas or depositing a material on said areas; and
- f. blank exposing the resist image and stripping it from the resist in aqueous alkali.

The invention further concerns a process for a positive resist on a surface which process comprises:

- a. applying to said surface the surface of a solid, unexposed, photosensitive layer having a thickness of at least 0.3 mils (approximately 8 microns), said layer comprised of (a) a polymer chosen from the group consisting of compositions having a polymer backbone and pendant acid-labile groups which are bound directly or indirectly to the polymer backbone, said pendant acid-labile groups represented by the formula:



where $n=0-4$; R^1 is hydrogen or lower alkyl (up to about 6 carbon atoms); R^2 is lower alkyl (up to about 6 carbon atoms); and R^3 and R^4 independently are hydrogen or lower alkyl where the definition of lower alkyl includes the joining of R^1 and R^2 or R^1 and either R^3 or R^4 , or R^2 and either R^3 or R^4 to form a 5-, 6-, or 7-membered ring; (b) an initiator system that forms a catalytic amount of strong acid upon exposure to actinic radiation having a wavelength between about 3000Å to about 9000Å, and (c) optionally, plasticizers, colorants and adhesion promoters, surfactants, the other surface of the layer having adhered thereto with low to moderate adherence a thin, flexible, polymer film support; then in either order;

- b. exposing the layer, imagewise, to actinic radiation to form an image;
- c. stripping the film support from the resulting image-bearing layer; and then,
- d. washing away the exposed areas of the layer to form a positive resist image;
- e. permanently modifying the adjacent areas on the substrate surface which are unprotected by the resist image by using a reagent capable of etching said areas or depositing a material on said area, and, without the need to apply a second coating of photosensitive material;
- f. imagewise exposing the resist layer again to form a second latent image;
- g. washing away the exposed areas of the layer to form a positive resist image;

6

- h. permanently modifying the adjacent areas on the substrate surface which are unprotected by the resist image by using a reagent capable of etching said areas or depositing a material on said area;
- i. solubilizing the resist and stripping it from the substrate.

DETAILED DESCRIPTION OF THE INVENTION

This invention is based on the discovery that polymers with pendant acid labile α -alkoxy alkyl esters of carboxylic acids or α -alkoxyalkyl ethers of 4-hydroxybenzyl esters can unexpectedly be made into stable high resolution fully aqueous developable positive acting dry film photoresists which are capable of withstanding both acid and alkaline processes typically used in the formation of printed circuits and have the capacity to protect holes in the substrate by tenting them.

Tenting is the process of forming a pad of resist over a hole in the substrate. It is surprising that these uncross-linked positive resists would survive the hot alkaline high pressure sprays typically used to develop dry film resists considering the high level of photocrosslinking required for the survival of tents made using negative resists. A distinct advantage of the positive dry film resists of the present invention that becomes clear with this discovery is that the formulation can be optimized for tenting independent of exposure, since the tents themselves are not exposed in making the image. In making the image, exposures can be set for optimum reproduction of the artwork because there is no exposure requirements for the tents.

In order to be developed after exposure, the resists described in the prior art which were based on polymers with pendant α -alkoxyalkyl ethers of phenols required aqueous alkaline solutions containing flammable alcohols. Surprisingly, the resists based on the phenolic α -alkoxyalkyl ethers of 4-hydroxy benzyl esters of the present invention are soluble in all aqueous alkali after exposure.

The dry film resists of the current invention are formulated to flow at about 100° C. so that they can be laminated to substrates under heat and pressure. When resists were made with acid labile *t*-butyl esters of carboxylic acids, as described in the prior art, heating to 100° C. after exposure was required to solubilize the polymer. The resulting developed image had distorted line edges. Resists of the current invention based on α -alkoxyalkyl esters of carboxylic acids can be solubilized after exposure by holding at room temperature for a brief period or by mild heating at less than 100° C. The developed images have sharp line edges.

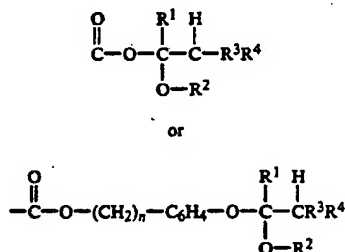
Finally, the resists of the present invention, when properly formulated, will withstand aqueous acid and alkaline etching and plating processes and even strongly alkaline processes such as electroless copper plating baths, yet they are developable and strippable in all aqueous alkali. A subsequent re-exposure and development of the original image to form a second image or a blank re-exposure and development for stripping is still possible.

POLYMERIC MATERIAL

The polymers used in these resists have pendant acid labile groups which are bound directly or indirectly to the polymer backbone. Acrylic, vinyl, polyester, and polyurethane backbones are all possible.

The polymeric materials of the present invention are made by methods known in the art. The polymers can be prepared by free radical polymerization, Group Transfer polymerization, or by other polymerization methods known in the art. The pendant acid labile groups may be selectively attached to the polymer backbone as part of the monomeric components used to form the backbone or after the backbone has been formed. Typically, monomeric components each containing an acid labile group (or sites to which such groups may be later attached) are copolymerized in suitable proportions to produce the polymeric material. Additional conventional monomer components may be incorporated in the copolymerization process to further modify polymeric material characteristics, e.g., to change the hardness, T_g, and the like.

The pendant acid labile groups useful in the compositions of this invention can be described by the formulae:



where n is 0 to 4; R¹ is hydrogen or lower alkyl; R² is lower alkyl; and R³ and R⁴ independently are hydrogen or lower alkyl where the definition of lower alkyl includes alkyl groups having 1 to 6 carbon atoms and the joining of R¹ and R², or R¹ and either R³ or R⁴, or R² and either R³ or R⁴ to form a 5-, 6-, or 7-membered ring. Some examples of acid labile monomeric components that fall within the scope of the invention when used to prepare the polymeric material are:

- 1-ethoxyethyl methacrylate (or acrylate),
- 1-butoxyethyl methacrylate (or acrylate),
- 1-ethoxy-1-propyl methacrylate (or acrylate),
- tetrahydropyranyl methacrylate (or acrylate),
- tetrahydropyranyl p-vinylbenzoate,
- 1-ethoxy-1-propyl p-vinylbenzoate,
- 4-(2-tetrahydropyranyloxy)benzyl methacrylate (or acrylate),
- 4-(1-butoxyethoxy)benzyl methacrylate (or acrylate).

Additional conventional monomer components (having no pendant acid labile groups) which may be used to modify the polymeric material include, but are not limited to, acrylic alkyl esters such as methyl methacrylate; ethyl methacrylate; 2-ethyl hexyl methacrylate; propyl methacrylate; cyclohexyl methacrylate; butyl methacrylate; benzyl methacrylate; benzyl acrylate; methyl acrylate; ethyl acrylate; propyl acrylate; butyl acrylate; styrene; acrylic alkyl amides such as N-butylacrylamide; N-octylacrylamide; acrylonitrile, styrene, p-methyl styrene; butadiene, isoprene. Preferred monomers for resistance to alkaline processing solutions include aromatic monomers such as styrene or benzyl methacrylate or hydrophobic aliphatic monomers such as 2-ethylhexyl, butyl or cyclohexyl methacrylate. Small quantities (typically less than 5 mole %) of glycidyl methacrylate may be added as an adhesion promoter.

PHOTOSENSITIVE ACID GENERATOR

Examples of compounds and mixtures which can be used as photoacid generators include diazonium, phosphonium, sulfonium and iodonium salts; halogen compounds organometal/organohalogen combinations; benzoin and o-nitrobenzyl esters of strong acids, e.g., toluene sulfonic acid; and N-hydroxy amide and N-hydroxyimide sulfonates as disclosed in U.S. Pat. No. 4,371,605. Also included are aryl naphthoquinonediazide-4-sulfonates. Preferred photosolubilizing agents are the diaryliodonium or triarylsulfonium salts. These are generally present in the form of salts with complex metal halides ions such as tetrafluoroborate, hexafluoroantimonate, hexafluoroarsenate, and hexafluorophosphate.

Another useful group of photosensitive acid generators include oligomers and polymers comprising appended anionic groups having an aromatic onium acid photogenerator as the positive counter ion. Examples of such polymers include those described in U.S. Pat. No. 4,661,429, column 9, lines 1 to 68, and column 10, lines 1 to 14, incorporated herein by reference.

It may be desirable to add a sensitizer to the system to adjust the spectral sensitivity to the available wavelength of actinic radiation. The need will depend on the requirements of system and the specific photosensitive compound used. For example, iodonium and sulfonium salts that only respond to wavelengths below 300 nm may be sensitized to longer wavelengths using benzophenone and derivatives thereof, polycyclic aromatic hydrocarbons such as perylene, pyrene, and anthracene, and derivatives thereof. The decomposition of diaryliodonium and triarylsulfonium salts has also been sensitized by bis-(p-N,N-dimethylaminobenzyliden)-acetone. Anthracene bound sulfonium salts, with chain lengths of three to four atoms, are efficient photosolubilizing agents. These compounds, which are disclosed in M. G. Tilley, Ph.D. Thesis, North Dakota State University, Fargo, N. Dak. (1988) [Diss. Abstr. Int. B, 49, 3791 (1989); Chem. Abstr., 111, 39942u], are a preferred class of photosolubilizing agents. Another preferred acid generator is ATASS, i.e., 3-(9-anthracenyl)propyl-diphenylsulfonium-, hexafluoroantimonate. In this compound the anthracene and the sulfonium salt are bonded by a three carbon chain. Additional examples of acid generator that may be used herein are diphenyliodonium tosylate, benzoin tosylate, and triarylsulfonium hexafluoroantimonate.

The amount of acid generator in the photoresist composition should generally be as low as possible without unduly sacrificing sensitivity, generally from about 0.1% to about 10% by weight of the photoresist composition. Less than about 0.1% generally lead to insensitive compositions while weight percentages greater than about 10% produce compatibility and control problems. For most acid-labile polymers, 0.5 to 6% by weight acid generator in the photoresist composition is preferred.

A sufficient amount of acid labile ester in the polymer is necessary to allow the exposed areas of the resist to be developable in all aqueous base either by dissolution or dispersion. Preferred all aqueous developing solutions include, but are not limited to 0.5% sodium hydroxide or 1.0% sodium carbonate. The addition of small amounts of surfactants or defoamers can be useful to aid development or to control foaming in the solution. The exact amount of acid labile ester depends on the resist

formulation, the polymer composition and molecular weight, and the glass transition of both. Experiments have demonstrated that as little as 25 mole % of tetrahydropyranyl methacrylate in a tetrahydropyranyl methacrylate/butyl methacrylate copolymer was sufficient for all aqueous development in 0.5% sodium hydroxide solution.

The Tg of the resist composition has to be adjusted so that it is within a useful range. The resist cannot be excessively tacky or flowable at room temperature at the lower end of the range and yet it must be able to flow at typical lamination temperatures of 100° to 110° C. at the upper end of a temperature range. A preferred range for the glass transition of the composition would be 15° C. to 60° C. The Tg of the polymer would have to fit within that range if it comprises the bulk of the resist although it could be higher providing that it can be plasticized so that the dry film resist falls within that range. Further, it is possible to add other monomers or additives such as polyketals and acetals, plasticizers and/or crosslinkers into the resist composition to modify certain properties.

COLORANTS

Colorants such as dyes and pigments are useful adjuncts in dry film photoresists because the developed resist image can be inspected for defects and a determination of when the resist has been cleaned from the substrate during development is possible. A preferred example of a colorant is Victoria Green dye. This material imparts a deep green color to a resist and upon exposure of the resist, it lightens in color in the irradiated areas. This creates an image of the artwork which is useful for inspecting the exposed sample for defects that might have been present in the artwork or dirt that accidentally was present during the exposure. Additives that create a visible image by forming a color or by a color change, e.g., leucolactones, would also be useful.

PRINTED CIRCUIT MANUFACTURE

Photoresists are used in temporary coatings in a primary imaging process to make printed circuits. In practice, a photoresist layer, typically between 8 and 125 microns thick, is applied to a printed circuit substrate which typically is a copper clad fiberglass epoxy board. The applied photoresist layer is then imagewise exposed to actinic radiation to solubilize exposed areas. The exposed areas are then completely removed typically with a developer solution which selectively dissolves, strips or otherwise disperses the exposed areas without

adversely affecting the integrity or adhesion of the unexposed areas. The surface areas of the substrate which were uncovered by the development process are then modified by etching or removing material therefrom or depositing a material thereon.

In the instance of primary imaging to form a printed circuit board, the uncovered copper surface areas may be etched or removed to form a printed circuit directly, or additional copper or other metal resistant to etchant, e.g., gold, tin/lead, etc., may be plated thereover. In the first instance, the unexposed resist is typically removed from the remaining copper surface by a stripping process involving re-exposure to actinic radiation followed by a second development operation to form the circuit board directly. In the second instance, the unexposed resist is first removed from the unplated copper surface which is then etched or removed from the substrate to form a plated printed circuit board.

DRY FILM RESIST LAMINATION

A pre-formed, dry-film, photosolubilizable resist layer typically is applied from a multi-ply, transfer, resist element using the lamination process as described in U.S. Pat. No. 4,193,797. The multi-ply, resist element comprises, in order, temporary support film, e.g., polyethylene terephthalate, a thin photosolubilizable resist layer, and optionally a removable cover sheet, e.g., polyethylene, to protect the resist element during storage. As described in the patent, the cover sheet, if present, is first removed and the uncovered photoresist surface is laminated to the surface of a copper clad printed circuit substrate using heat and/or pressure, e.g., with a conventional hot-roll laminator. Although the laminate may be imagewise exposed to actinic radiation through the temporary support film, in most instances, where the photoresist layer is insensitive to ambient conditions and is not excessively tacky, the temporary support is removed before imaging to improve resolution and other such properties. In some instances resist adhesion to the substrate can be improved by treating the substrate surface with a liquid at or just prior to lamination such as a solution of adhesion promoters as disclosed in Jones, U.S. Pat. No. 3,645,772 a solvent or swelling agent for the resist layer as disclosed in Fickes. The liquid in some instances may be photosensitive such as the photoresist solutions disclosed in Isaacson, U.S. Pat. No. 3,629,036. The resist may also be applied to the substrate with a vacuum laminator.

TABLE I

| POLYMER COMPOSITION AND DATA | | | | | | | |
|------------------------------|---|---------|---------|----------------|----------------|--------------------|--------------------|
| # | Polymer Composition | Molar % | Prep | M _w | M _n | T _g °C. | T _d °C. |
| 1 | Tetrahydropyranyl methacrylate/butylmethacrylate | 22:78 | GTP | 20,800 | 19,600 | 49 | |
| 2 | Tetrahydropyranyl methacrylate/benzylmethacrylate | 50:50 | GTP | 36,000 | 21,500 | | 185 |
| 3 | Poly(tert-butyl acrylate) | 100 | | | 100,000 | | |
| 4 | Poly(tert-butylmethacrylate) | 100 | | | 50,000 | | |
| 5 | Novolak Resin HRJ 1829 | | | | | | |
| 6 | THP derivative of HRJ 1829 | | | | | 61 | 148 |
| 7 | Poly(4-(2-tetrahydropyranyloxy)benzylmethacrylate) | 100 | GTP | 11,500 | 9,390 | 62 | 251 |
| 8 | Tetrahydropyranyl-methacrylate/benzyl methacrylate methacrylic Acid | 46:51:3 | RADICAL | 183,000 | 58,500 | | |
| 9 | Poly(tetrahydropyranyl-methacrylate) | 100 | GTP | 20,000 | 13,000 | 91 | 174 |
| 10 | Tetrahydropyranyl-methacrylate/block-benzyl | 50:50 | GTP | 36,400 | 23,400 | 80 | 177 |

TABLE 1-continued

| POLYMER COMPOSITION AND DATA | | | | | | |
|------------------------------|---|-----------|---------|----------------|----------------|---------------------------------------|
| # | Polymer Composition | Molar % | Prep | M _w | M _n | T _g °C. T _d °C. |
| 11 | methacrylate | | | | | |
| 11 | 2-Tetrahydrofuranyl-methacrylate/benzyl methacrylate | 50:50 | GTP | 12,300 | 10,200 | 80 187 |
| 12 | Tetrahydropyranyl-methacrylate/benzyl methacrylate | 40:60 | GTP | 26,100 | 17,300 | 70 187 |
| 13 | Tetrahydropyranyl-methacrylate/2-ethylhexyl methacrylate/benzylmethacrylate | 33:40:27* | GTP | 25,800 | 13,800 | 58 189 |
| 14 | Tetrahydropyranyl-methacrylate/2-ethylhexyl methacrylate/benzylmethacrylate | 39:32:29* | GTP | 27,000 | 14,900 | 68 194 |
| 15 | Ethoxypropyl-methacrylate/benzyl methacrylate | 50:50 | RADICAL | 54,700 | 21,200 | 58 196 |

* wt. %

In the following preparations, gel permeation chromatography (GPC) is used with polystyrene standards for molecular weight measurements. Differential scanning calorimetry is abbreviated DSC. Procedures for carrying out group transfer polymerizations (drying of apparatus, purification of monomers) are as described in Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* 1987, 20, 1473.

POLYMER #1

Poly(n-butyl methacrylate (78 mole %)

THPMA (22 mole %))

Tetrahydropyranyl methacrylate (THPMA) and n-butyl methacrylate were purified separately by passage over a column of basic alumina under argon. To a solution of 1.48 mL (5 mmol) of 1-(2-trimethylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene and 0.1 mL of tetrabutylammonium biacetate (0.04 M in THF) in 150 mL of THF under an argon atmosphere was added a mixture of 64.1 g (71.7 mL, 0.45 mol), of n-butyl methacrylate and 21.6 g (21.2 mL, 0.127 mol) of THPMA at a rate such that the temperature of the reaction remained between 35° and 40° C. NMR analysis of the reaction mixture showed no residual monomer. Precipitation in methanol gave an oil, which, after drying at 0.1 mm, solidified to 60 g of poly(n-butyl methacrylate [78 mol%], THPMA [22 mol%]). GPC: M_n=19,600, M_w=20,800, M_w/M_n=1.11. DSC: T_g=49.2° C.

POLYMER #2

Preparation of 1:1 Random Copolymer of Tetrahydropyranyl Methacrylate and Benzyl Methacrylate by Group Transfer Polymerization

To a solution of 0.45 mL (2.5 mmol) of 1-(2-trimethylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene (TTEB) and 0.4 μL of tetrabutylammonium biacetate hexahydrate (0.005 M in tetrahydrofuran) in 75 mL of tetrahydrofuran (THF) under argon was added a mixture of 15 mL (14.78 g, 0.084 mol) of benzyl methacrylate and 14 mL (14.28 g, 0.084 mol) of THPMA at a rate such that the temperature did not exceed 36° C. Both monomers had been individually passed over columns of basic alumina under an argon atmosphere just prior to use. NMR analysis of an aliquot of the reaction mixture showed 8% residual monomer. The product was precipitated in methanol and dried at room temperature to give 29.7 g of poly(THPMA-co-benzyl methacrylate). GPC: M_n=21,500, M_w=36,000, M_w/M_n=1.67

(polystyrene standard). NMR analysis of the copolymer shows the composition to be 1:1 on a molar basis.

POLYMER #3

Poly(tert-butyl acrylate), 35% in toluene purchased from Monomer-Polymer Laboratories, Trevose, Pa. 19047.

POLYMER #4

Poly(tert-butyl methacrylate) purchased from Monomer Polymer Laboratories.

POLYMER #5

Phenolic Novolak Resin HRJ 1829, Novolak for flexible photoresist, mp 140° C. obtained from Schenectady Chemicals, Inc., Schenectady, N.Y.

POLYMER #6

Preparation of tetrahydropyranyl Novolak HRJ 1829

A mixture of 5.09 g of Novolak HRJ-1829, 20 mL of 3,4-dihydro-2H-pyran, and 0.1 g of pyridine hydrochloride was stirred at reflux for 18 hr. Then 1 g of cross-linked poly(dimethylaminomethylstyrene) was added, and the mixture was stirred for 1 hr and filtered. Precipitation of the product from the filtrate with methanol gave, after drying in vacuo at room temperature, 6.5 g of tetrahydro-2-pyranyl ether of Novolak resin. ¹H NMR (300 MHz) shows a resonance at δ 5.35 ppm characteristic of the methine proton of a tetrahydropyranyl ether. DSC: T_g 60.8° C. with decomposition endotherm at 148.09° C. (335.6 J/g). TGA shows 29.45% weight loss at 161.95° C.

POLYMER #7

Poly(4-tetrahydropyranyloxybenzyl methacrylate)

To a solution of 0.64 mL (2 mmol) of 1-(2-trimethylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene, 0.55 mL of tetrabutylammonium biacetate (0.04 M in THF), and 0.06 mL of bis(dimethylamino)methylsilane in 40 mL of THF was added dropwise a solution of 20 g (72.5 mmol) of 4-tetrahydropyranyloxybenzyl methacrylate (purified by passing over a column of basic alumina in hexane solution, followed by evaporation of the hexane under reduced pressure) in 30 mL of THF. When the exothermic polymerization was finished, and the temperature had returned to room temperature, the reaction mixture was poured into methanol. Filtration gave 19 g of poly(4-tetrahydropyranyloxybenzyl methacrylate). GPD: M_n=9390, M_w=11,500, M_w/M_n=1.23.

13

DSC: $T_g = 62.3^\circ \text{C}$, with a decomposition endotherm at 250.5°C . TGA: rapid loss of 24.74% of weight at 248.1°C . The monomer was prepared from methyl 4-hydroxybenzoate by reaction with an excess of 3,4-dihydro-2H-pyran in the presence of sulfuric acid catalyst to give methyl 4-(2-tetrahydropyranyloxy)benzoate, which was then reduced with lithium aluminum hydride in THF solution to give 4-(2-tetrahydropyranyloxy)benzyl alcohol. Esterification with methacrylyl chloride and triethylamine in dichloromethane solution gave 4-tetrahydropyranyloxybenzyl methacrylate, m.p. 36°C .

POLYMER #8

Poly(benzyl methacrylate [51 mol%]-co-tetrahydropyranyl methacrylate [46 mol%]-co-methacrylic acid [3 mol%])

A solution of 24.4 mL (0.141 mol) of benzyl methacrylate, 23.4 mL (0.141 mol) of THPMA, and 75 mg of azobisisobutyronitrile (VAZO 64) was heated at 75°C under argon for 7 hr, during which time the solution became viscous. An additional 75 mg of VAZO 64 (dissolved in 5 mL of ethyl acetate) was added, and heating at 75°C was continued for 5 hr. NMR analysis of the solution showed about 8.5% residual monomer(s). The product was isolated by precipitation in methanol. Titration of an aliquot of the product with standard sodium hydroxide solution showed 0.18 meq/g of methacrylic acid units in the polymer. Thus, the product is poly(THPMA [46 mol%]-co-benzyl methacrylate [51 mol%]-co-methacrylic acid [3 mol%]). GPC: $M_n = 58,500$, $M_w = 183,000$, $M_w/M_n = 3.13$.

POLYMER #9

Poly(2-tetrahydropyranyl methacrylate)

To a solution of 0.15 mL (0.5 mmol) of 1-(2-trimethylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene and 30 μL of tetrabutylammonium biacetate (0.04 M in THF) in 30 mL of THF was added dropwise 10 g (9.8 mL, 58.8 mmol) of tetrahydropyranyl methacrylate (purified by passage over a column of basic alumina under an argon atmosphere). NMR analysis of the reaction mixture showed that there was no residual monomer. Precipitation with methanol gave 8.34 g of poly(2-tetrahydropyranyl methacrylate). GPC: $M_n = 13,600$, $M_w = 20,000$, $M_w/M_n = 1.47$.

POLYMER #10

Poly(2-tetrahydropyranyl methacrylate-b-benzyl methacrylate)

To a solution of 0.925 mL (2.9 mmol) of 1-(2-trimethylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene and 62.5 μL of tetrabutylammonium biacetate (0.04 M in THF) in 100 mL of THF was added dropwise 30.6 g (30 mL, 174 mmol) of 2-tetrahydropyranyl methacrylate at a rate such that the temperature remained between 35°C and 40°C . Four minutes after the temperature first began to drop following the addition of the 2-tetrahydropyranyl methacrylate, the addition of 31.8 g (31.25 mL, 174 mmol) was begun. After the addition was complete, NMR analysis of an aliquot of the reaction mixture showed that no residual monomer was present. Precipitation with methanol gave 62 g of poly(2-tetrahydropyranyl methacrylate-b-benzyl methacrylate). GPC: bimodal with 17% having $M_n = 7990$, $M_w = 8680$, $M_w/M_n = 1.09$, and 83% having

14

$M_n = 41,400$, $M_w = 42,100$, $M_w/M_n = 1.02$. DSC: $T_g = 80.3^\circ \text{C}$ with decomposition endotherm at 176.9°C . $^1\text{H-NMR}$ analysis of the product shows that the composition is 1:1 tetrahydropyranyl methacrylate:benzyl methacrylate.

POLYMER #11

Poly(2-tetrahydrofuranyl methacrylate-co-benzyl methacrylate)

To a solution of 0.74 mL (2.5 mmol) of 1-(2-trimethylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene and 175 μL of tetrabutylammonium biacetate (0.04 M in THF) in 75 mL of THF was added dropwise a mixture of 25.4 g (25.0 mL, 145 mmol) of benzyl methacrylate and 22.6 g (21.3 mL, 145 mmol) of 2-tetrahydrofuranyl methacrylate. Analysis of an aliquot of the reaction mixture showed the presence of residual monomers. Precipitation with methanol gave 19.3 g of poly(2-tetrahydrofuranyl methacrylate-co-benzyl methacrylate). $^1\text{H-NMR}$ analysis of the polymer showed the molar composition to be 1:1 tetrahydrofuranyl methacrylate:benzyl methacrylate. GPC: $M_n = 10,200$, $M_w = 12,300$, $M_w/M_n = 1.20$. DSC: $T_g = 80.4^\circ \text{C}$ with a broad, complex decomposition endotherm of $182.8^\circ\text{--}251^\circ \text{C}$. TGA: 16.3% weight loss at 186.7°C .

POLYMER #12

Poly(tetrahydropyranyl methacrylate [40 mol%]-co-benzyl methacrylate [60 mol%])

To a solution of 0.78 mL (2.46 mmol) of 1-(2-trimethylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene and 700 μL of tetrabutylammonium biacetate (0.04 M in THF) in 130 mL of THF was added dropwise a mixture of 19.6 g (19.2 mL, 115.6 mmol) of tetrahydropyranyl methacrylate and 30.5 g (30.0 mL, 173.4 mmol) of benzyl methacrylate at a rate such that the temperature remained near 45°C during the addition. Precipitation with methanol gave 50 g of poly(tetrahydropyranyl methacrylate-co-benzyl methacrylate). $^1\text{H-NMR}$ analysis of the product shows the composition to be 40 mole% tetrahydropyranyl methacrylate, 60 mole% benzyl methacrylate. GPC: $M_n = 17,300$, $M_w = 26,100$, $M_w/M_n = 1.51$. DSC: $T_g = 70.1^\circ \text{C}$ with a decomposition endotherm at 186.9°C . TGA: 16.02% weight loss at 184.4°C .

POLYMER #13

Poly(tetrahydropyranyl methacrylate [33 wt%]-co-2-ethylhexyl methacrylate [40 wt%]-co-benzyl methacrylate [27 wt%])

THPMA, 2-ethylhexyl methacrylate, and benzyl methacrylate were purified by passage over a column of basic alumina under argon. To a solution of 0.44 mL (1.5 mmol) of 1-(2-trimethylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene and 0.08 mL of tetrabutylammonium biacetate (0.04 M in THF) in 100 mL of THF was added a mixture of 9.9 g (9.7 mL, 58.2 mmol) THPMA, 12 g (13.6 mL, 60.6 mmol) of 2-ethylhexyl methacrylate, and 8.1 g (8.2 mL, 46 mmol) of benzyl methacrylate at a rate such that the temperature remained below 30°C . When the monomer mixture had been added, addition of 0.03 mL of tetrabutylammonium biacetate (0.04 M in THF) resulted in a temperature rise of 7°C . NMR analysis of the reaction mixture showed the presence of a trace of unreacted monomers. Successive precipitation in methanol and in hexane

15

cooled at -78°C . followed by drying gave 23.1 g of solid poly(THPMA [33 wt%]-co-2-ethylhexyl methacrylate [40 wt%]-co-benzyl methacrylate [27 wt%]). GPC: $M_n=13,800$, $M_w=25,800$, $M_w/M_n=1.87$. DSC: $T_g=57.6^{\circ}\text{C}$. with a decomposition endotherm peaking at 188.0°C .

POLYMER #14

Poly(tetrahydropyranyl methacrylate [39 wt%]-co-2-ethylhexyl methacrylate [32 wt%]-co-benzyl methacrylate [29 wt%])

Tetrahydropyranyl methacrylate (11.7 g), 9.6 g of 2-ethylhexyl methacrylate, and 8.7 g of benzyl methacrylate were polymerized using the general procedure used for polymer #13 (with precipitation in cold methanol) to give 25.5 g of poly(THPMA [39 wt%], 2-ethylhexyl methacrylate [32 wt%], benzyl methacrylate [25 wt%]). GPC: $M_n=14,900$, $M_w=27,000$, $M_w/M_n=1.81$. DSC: $T_g=67.7^{\circ}\text{C}$. with a decomposition endotherm peaking at 194.1°C .

POLYMER #15

Poly(1-ethoxypropyl methacrylate-co-benzyl methacrylate)

To a refluxing mixture of 150 mL of deoxygenated ethyl acetate, 25.43 g (144.5 mmol) of benzyl methacrylate, and 24.89 g (144.5 mmol) of 1-ethoxypropyl methacrylate (prepared by the acid-catalyzed reaction of ethyl 1-propyl ether and methacrylic acid) under argon, was added 0.15 g of azobis(isobutyronitrile). After refluxing for 8 hr, the solution was treated with an additional 0.15 g of azobis(isobutyronitrile), and refluxing was continued for 18 hr. NMR analysis of the reaction mixture showed the presence of 4% unreacted monomers. Precipitation in methanol gave 49.4 g of poly(1-ethoxypropyl methacrylate-co-benzyl methacrylate). ^1H -NMR analysis of the product shows the composition to be 1:1 1-ethoxypropyl methacrylate:benzyl methacrylate. GPC: $M_n=21,200$, $M_w=54,700$, $M_w/M_n=2.57$. DSC: $T_g=58.1^{\circ}\text{C}$. with a decomposition endotherm at 195.5°C . TGA: 19.8% weight loss at 187.7°C .

INITIATORS

Initiator #1—Cyracure 6974 manufactured by Union Carbide

Initiator #2—Benzoin Tosylate obtained from Ciba Geigy

Initiator #3—Dimethyl-2-(4-hydroxynaphthyl)sulfonium hexafluorophosphate

REF: prepared in accordance with the general procedure described in U. V. Crivello and H. J. W. Lam, J. Poly. Sci., Polym. Chem. Ed., 18, 1021, (1980).

Initiator #4—[3-(9-anthracenyl)propyl]diphenylsulfonium hexafluoroantimonate

Ref: Mark Gerard Tilley, North Dakota State University PhD Thesis, "Synthesis and Reactivity of Cationic Photoinitiators and Translational Diffusion of Small Molecules in Polymers, October, 1988.

Procedure for Treatment of Copper Clad Panels with Benzotriazole

A solution was prepared comprising 385 grams of deionized water, 47.5 grams of 37% hydrochloric acid, and 47.5 grams of benzotriazole. A working solution was prepared by mixing one part of this solution to 9 parts of deionized water.

16

The copper clad glass epoxy panels were scrubbed and dried. They were dipped for 15 seconds into the working benzotriazole solution, rinsed for 30 seconds in a stream of deionized water, and dried in oil free air. The panels are then ready to laminate with resist.

To further illustrate the present invention the following examples are provided.

EXAMPLES

EXAMPLE 1

Two photoresist coating solutions 1A 1B, and 1C were prepared with the ingredients as listed below:

| | 1A | 1B |
|-----------------------------------|---------|---------|
| Polymer #1 [poly(THPMA/ButylMA)] | 1.5 g | |
| Polymer #2 [poly(THPMA/BenzylMA)] | | 1.5 |
| Cyracure 6974 | 0.1 g | 0.1 g |
| Chlorothioxanthone | 0.01 g | 0.01 g |
| Benzophenone | 0.24 g | 0.24 g |
| Dibutylphthalate | | 0.20 g |
| Victoria Green Dye | 0.001 g | 0.001 g |
| Methylcelketone | 3.0 g | 3.0 g |

DRY FILM RESIST

Solution 1A, prepared with a copolymer of tetrahydropyranyl methacrylate and n-butyl methacrylate, was coated onto 92 gauge polyester film and air dried to give a green resist film 1 mil thick. The coating was then laminated to a scrubbed copper clad epoxy panel at 105°F . and 2 fpm using a Du Pont HRL hot roll laminator. On a sample of the panel different areas were given exposures of 50, 100, 200, 400 and 600 mj/cm^2 using a Du Pont PC 130 printer (containing a 5000 W Sylvania M061 lamp). The exposures were held 15 minutes at room temperature prior to being developed in a 0.5% aqueous sodium hydroxide solution at 105°F . in an ASI spray developer unit at 30 psi. The exposure energy incident upon the samples was checked with an IL 770 radiometer which integrated energy between 300 and 400 nanometers. The 200 mj/cm^2 and higher exposures allowed the resist to be developed at 150 seconds. Another sample was exposed imagewise at 200 mj/cm^2 through a UGRA Plate Control Wedge 1982 containing concentric circles spaced from 4 to 70 microns (available from the Graphic Arts Technical Foundation) and held 15 minutes at room temperature. The green color in those areas which had received exposure was substantially faded, providing a crisp bleach out image of the artwork. The developed sample held and resolved 55 micron lines and spaces and the edges of the image lines were even and well formed.

Solution 1B was prepared using a copolymer of tetrahydropyranyl methacrylate and benzyl methacrylate. A one mil dry film was coated and laminated to scrubbed copper clad glass epoxy which had been previously scrubbed and treated with a benzotriazole solution as described in the procedure for treatment of copper clad glass epoxy with benzotriazole. On a sample of the panel different areas were given exposures of 100, 200, 300, 400 and 800 mj/cm^2 held for 30 minutes at room temperature, and developed in a beaker of 0.5% sodium hydroxide at 105°F . The 400 mj exposure developed clean at 290 seconds and the 800 mj exposure at 47 seconds. No heat was required. At exposures of 200 mj/cm^2 and 400 mj/cm^2 the resist developed in the same

solution in the ASI 30 psi spray developer at 60 seconds and 7 seconds respectively.

COMPARATIVE EXAMPLE

Two photoresist coating solutions 2A and 2B were prepared with the ingredients listed below:

| | 2A | 2B |
|---|---------|---------|
| Polymer #3 [poly(t-butyl acrylate)] | 1.5 g | |
| Polymer #4 [poly(t-butyl methacrylate)] | | 1.5 g |
| Cyrcure 6974 | 0.1 g | 0.1 g |
| Chlorothioxanthone | 0.002 g | 0.002 g |
| Benzophenone | 0.24 g | 0.24 g |
| 2-Methoxypropane | 3.0 g | |
| Methylethylketone | | 3.0 g |

DRY FILM RESIST

Solution 2A, prepared with poly(t-butyl acrylate), was coated onto 92 gauge polyester film with a six mil doctor knife and air dried to give a film 1 mil thick. One part of this coating was laminated to a panel of scrubbed copper clad epoxy laminate at 105° C. at 2 fpm; another part was laminated to a panel of laminate which had been previously scrubbed and treated with a benzotriazole solution as described in Example 1. The polyester was removed and different areas of each sample were given separate exposures of 600, 1200 and 2400 mj/cm² as indicated in the table below. One sample at each exposure was placed in a 100° C. oven for two minutes and then held for an additional 13 minutes prior to development. The other sample at each exposure was placed in the 100° C. oven for 15 minutes. All of the samples were subjected to spray development in an ASI unit with 0.5% sodium hydroxide solution at 105° F. and 30 psi spray pressure until they developed clean (as determined by a brief etch in acidic ammonium persulfate) or for a maximum contact time of 10 minutes. The times to develop cleanly are summarized in the table (DNC means incomplete development which left resist on the copper).

TABLE

| Comparative Example | | | | | | |
|---------------------|--------|---------|---------------------------|---------|---------|---------|
| Coating on copper | | | Coating on treated copper | | | |
| Exp. | 600 mj | 1200 mj | 2400 mj | 600 mj | 1200 mj | 2400 mj |
| 2 min. in oven | DNC | DNC | DNC | DNC | DNC | 120 sec |
| 15 min. in oven | DNC | DNC | 120 sec | 120 sec | 120 sec | 120 sec |

Samples of coating 2A laminated to the treated copper were imaged exposed through the UGRA target at 600 and 1200 mj/cm², heated for 15 minutes at 100° C. and developed for 130 seconds in the ASI spray developer. Although both images held and resolved 55 micron lines, the developed edges of isolated lines were uneven and ragged.

LIQUID RESIST

Solution 2B, prepared with poly(t-butylmethacrylate), was coated onto 92 gauge polyester to give a very brittle coating which shattered. To test the resist, solution 2B was coated directly onto a panel of scrubbed copper clad epoxy laminate with a six mil doctor blade, air dried, and further dried in a 40° C. oven for 15 minutes to give a coating one mil thick. An exposure of 600 mj/cm² followed by heating at 100° C. for 15 minutes allowed this resist to be developed clean in 150 seconds under the conditions previously cited. The edges of

isolated lines on an imaged sample produced under these conditions were uneven and ragged.

COMPARATIVE EXAMPLE

Three photoresist coating solutions 3A, 3B and 3C were prepared with the ingredients listed below. Polymers 5 and 6 are included for comparison. Polymer 7 is within the invention.

| | 3A | 3B | 3C |
|------------------------------|---------|---------|---------|
| Polymer #5 | 1.5 g | | |
| [Novolak Resin HRJ1829] | | | |
| Polymer #6 | | 1.5 g | |
| [THP derivative of HRJ1829] | | | |
| Polymer #7 | | | 1.5 g |
| [poly(4-(2-THPOxy)benzylMA)] | | | |
| Cyrcure 6974 | 0.1 g | 0.1 g | 0.2 g |
| Chlorothioxanthone | 0.002 g | 0.002 g | 0.002 g |
| Benzophenone | 0.24 g | 0.24 g | 0.24 g |
| Dibutylphthalate | 0.2 g | 0.2 g | 0.2 g |
| Victoria Green Dye | 0.001 g | 0.001 g | 0.001 g |
| Methylethylketone | 3.0 g | 3.0 g | 3.0 g |

LIQUID COATING

Solution 3A was coated onto a piece of scrubbed copper clad glass epoxy with a six mil doctor blade, air dried, and fully dried in a 40° C. oven for 15 minutes to give a coating one mil thick. A sample was passed through the ASI developer unit with 0.5% sodium hydroxide at 105° F., but the coating would not wash clean after 10 minutes. Another sample was dipped into a stirred beaker with a 50/50 vol/vol solution of Shipley Microposit 351 (essentially 5% sodium hydroxide) and DI water at 105° F. The coating developed from the panel in 60 seconds. A third sample developed clean in 19 seconds when placed in a semi-aqueous developer solution at 105° F. comprising 70 grams of n-propyl alcohol, 128 grams of water, and 2 grams of potassium hydroxide.

DRY FILM RESIST

A second sample of HRJ1829 was converted to its tetrahydropyranyl ester derivative using dihydropyran (Polymer #6). A coating solution 3B was prepared identical to 3A, except that the tetrahydropyranyl derivative replaced the HRJ1829 polymer; the solution was coated onto one mil polyester with a six mil doctor blade and air dried to give a one mil thick dry film resist. This photosensitive coating was laminated onto scrubbed and treated copper clad epoxy laminate with a hot roll laminator. Samples of the coating were given separate exposures of 100, 200, 400 and 800 mj/cm² and held for thirty minutes. During the hold time they received different heat treatments as listed in Table 3 below. The samples were immersed in all aqueous and semi-aqueous developer until the resist cleaned from the copper or for a maximum of 5 minutes. Note that this resist would only develop in semi-aqueous developer and then only after extensive heating.

TABLE 3

| Developer/ Temp | Hold Temp/ Time | 100 mj/cm ² | 200 mj/cm ² | 400 mj/cm ² | 800 mj/cm ² |
|--|---------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 351/H ₂ O 50/50 105° F. | RT | DNC | sl. dev | heavy residue | heavy residue |
| | 100° C./ 5 min. | DNC | sl. dev | heavy residue | heavy residue |
| | 100° C./ 15 min. | DNC | DNC | heavy residue | heavy residue |
| Semi-Aqueous 105° C. | RT | DNC | heavy residue | heavy residue | heavy residue |
| | 100° C./ 5 min. | DNC | heavy residue | heavy residue | heavy residue |
| | 100° C./ 15 min. | DNC | scum | 210 sec | 45 sec |

Two samples of coating 3B were imagewise exposed through the UGRA artwork at 400 and 800 mj/cm², held 15 minutes, heated for 15 minutes at 100° C., and developed in the semi-aqueous developer at 105° F. The images developed cleanly, but the line edges were ragged and uneven.

DRY FILM RESIST

For comparison, a one mil dry film was coated on 92 gauge polyester from solution 3C containing poly(4-(tetrahydropyranyloxy)-benzyl methacrylate) which is within the present invention, dried, and laminated to scrubbed and treated copper clad glass epoxy. An exposure of 200 mj/cm² allowed to resist to develop in a 50/50 Shipley Microposit 351 developer solution in 25 seconds at 105° F. The unexposed resist remained glossy. Unlike the resist containing tetrahydropyranyl derivative of the Novalak resin, this resist did not require heating after exposure and it developed in all aqueous alkali. A sample images through a UGRA target at 200 mj/cm² and developed at 25 seconds in the same developer held 70 micron lines.

EXAMPLE 4

Four photoresist coating solutions 4A, 4B, 4C and 4D were prepared with the ingredients listed below:

| | 4A | 4B | 4C | 4D |
|----------------------|---------|---------|---------|---------|
| Polymer #2 | 1.5 g | 1.5 g | 1.5 g | 1.5 g |
| Cyrcure 6974 | 0.1 g | | | |
| Chlorothioxanthone | 0.002 g | | | |
| Benzoin Tosylate | | 0.05 g | | |
| Initiator #3 | | | 0.1 g | |
| Initiator #4 | | | | 0.05 g |
| Benzophenone | 0.24 g | 0.24 g | 0.24 g | 0.24 g |
| Dibutylphthalate | 0.2 g | 0.2 g | 0.2 g | 0.20 g |
| Victoria Green Dye | 0.001 g | 0.001 g | 0.001 g | 0.001 g |
| Methylisobutylketone | 3.0 g | 3.0 g | 3.0 g | 3.0 g |

These solutions were coated onto one mil polyester with a six mil doctor blade and air dried to give one mil thick dry film resists. These were laminated onto scrubbed and benzotriazole treated copper clad epoxy laminate with a hot roll laminator. The green color of all four resists was bleached one exposure, providing a visible reproduction of the artwork in the resist. Resist 4A was given a 100 mj/cm² exposure, held 30 minutes at room temperature, and developed for 13 seconds to a step 2 (step density 0.15) after development for 13 seconds in 0.5% sodium hydroxide spray as previously described. Resist 4B developed to a step 2 at an exposure of 564 mj/cm² and a development time of 18 seconds. Resist 4C developed to a step 3 after 400

50 mj/cm² exposure and a development time of 13 seconds. Resist 4D developed in 15 seconds with a 100 mj/cm² exposure.

A sample of each of the laminated resists 4A, 4B and 4C were exposed through a fine line and space target and developed as indicated above. The samples were etched in ammonical cupric chloride, pH 8.4, s.g. 2.2, at 130° F. and 38 psi in a Chemcut spray etcher. The etched samples held isolated 55 micron etched lines and resolved 25 micron etched channels. The resist on these samples was then stripped by giving them 4 joules of UV exposure on a conveyORIZED exposure source, heating for 60 seconds at 160° C. on a conveyORIZED infrared unit, and passing them through the original spray developer for 60 seconds.

EXAMPLE 5

A sample of resist 4A from Example 4 was imaged with pads and developed as in the previous example. The sample was precleaned in a sodium persulfate/sulfuric acid bath for 60 seconds, followed by 10 seconds in 10% sulfuric acid and another 10 seconds in fluoboric acid. It was then plated for 15 minutes in a tin/lead fluoborate bath at 10 amps per square foot. The sample was then reimaged at 500 mj/cm² with a line pattern that intersected the plated pads and developed. The reimaged sample was etched in ammonical cupric chloride and stripped as previously described to give a sample with solder plated pads and copper conductors.

EXAMPLE 6

A sample of resist 1B was imaged with a fine line and space target as described in Example 4 and precleaned in a sodium persulfate/sulfuric acid solution. The sample was placed into a PCK-570 full build electroless copper bath at 72° C. and pH 12. The bath was replenished with formaldehyde and sodium hydroxide as needed over a period of 7½ hours to keep the bath actively depositing electroless copper in the developed channels of the resist where the copper cladding of the laminate had been uncovered. At the end of the time the resist had not blistered or lifted. The sample was dipped into warm sulfuric acid for 30 seconds and given 2 joules of UV exposure. The bulk of the resist was removed after 5 minutes in the ASI spray processor with 0.5% sodium hydroxide after 5 minutes.

EXAMPLE 7

Resist solution 7A was prepared by dissolving 3.0 grams of Polymer #8 prepared by free radical polymerization, 0.4 grams of dibutyl phthalate, 0.48 grams of benzophenone, 0.004 grams of chlorothioxanthone, 0.2 grams Cyrcure 6974, and 0.002 grams of Victoria Green dye into six grams of methylethyl ketone. A coating was drawn on 92 gauge polyester with a six mil doctor knife to give a 0.8 mil thick dry film resist after drying. Another coating was drawn with a 10 mil knife to give a resist 1.8 mils thick. These coatings were laminated to scrubbed copper clad epoxy laminate. The thinner resist developed clean at 12 seconds after an exposure 200 mj/cm²; the thicker resist developed clean in 15 seconds after an exposure of 400 mj/cm². These resists were laminated to both sides of scrubbed copper clad epoxy panels over a pattern of through holes in the laminate which were 34 mils and 96 mils in diameter. After passing through a 0.5% sodium hydroxide solution at 105° F. in an ASI spray developer at 30 psi spray pressure top and bottom for 15 seconds, the panel with

the 0.8 mil resist had 99% of the 34 mil tents intact. On the 1.8 mil resist, after 120 seconds under the same conditions, 80% of the 96 mil tents survived.

EXAMPLE 8

Solutions were prepared by dissolving 1.5 grams of the polymers in Table 5 below into 3 grams of methyl-ethyl ketone and coating the solution onto 92 gauge polyester with a six mil knife and air drying. An attempted lamination was then made with each of these coatings in the standard fashion for a dry film resist, they were passed through the nip of a Du Pont HRL hot roll laminator set at 105° C. at 2 fpm. along with a scrubbed piece of copper clad glass epoxy. The results of this trial, summarized in Table 5, indicate that the T_g of the coating must be below 60° to 70° C. for a proper lamination of the resist.

TABLE 5

| Polymer** | T _g | Lamination Result |
|-------------|----------------|--|
| Polymer #2 | 97° C. | Would not laminate, very brittle and badly cracked |
| Polymer #8 | 97° C. | Would not laminate |
| Polymer #9 | 91° C. | Would not laminate, very brittle and badly cracked |
| Polymer #10 | 80° C. | Only partial lamination, badly cracked |
| Polymer #11 | 80° C. | Laminated, but cracked |
| Polymer #12 | 70° C. | Mostly laminated, but cracked |
| Polymer #14 | 68° C. | Laminated, no cracks, but air entrapment* |
| Polymer #13 | 58° C. | Laminated, no cracks, air entrapment |
| Polymer #15 | 58° C. | Good lamination |
| Polymer #1 | 49° C. | Good lamination |

*Air entrapment is the condition where pockets of air are trapped at the interface of the resist and the uneven surface of the copper because of insufficient flow of the resist film at lamination

**All of the above polymers are within the invention but results identify preferred ranges of T_g for lamination

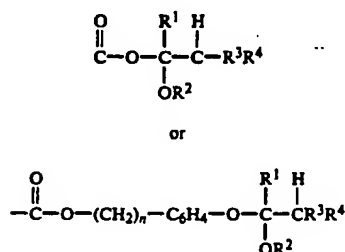
As many differing embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments except as defined in the appended claims.

Having described the invention, we now claim the following and their equivalents.

What is claimed is:

1. A dry film photoresist element comprising a thin flexible polymeric film support having adhered thereto with low to moderate adherence a solid photosensitive layer having a thickness of about 8 microns or greater, said layer comprising the following composition:

(a) a polymer chosen from the group consisting of compositions having a polymer backbone and pendant acid-labile groups which are bound directly or indirectly to the polymer backbone, said pendant acidlabile groups represented by the formula:



where R¹ is hydrogen, *r* lower alkyl; R² is lower alkyl; and R³ and R⁴ independently are hydrogen or lower alkyl where the definition of lower alkyl includes the joining of R¹ and R² or R¹ and either R³ or R⁴, or R² and either R³ or R⁴ to form a 5-, 6-, or 7-membered ring;

(b) an initiator system comprising an initiator or an initiator and at least one sensitizer that generates, upon exposure to actinic radiation having a wavelength between about 3000Å and about 9000Å, a catalytic amount of a strong acid.

2. The dry film photoresist element described in claim 1 wherein the solid photosensitive layer contains a plasticizer.

3. The dry film photoresist element described in claim 1 wherein the solid photosensitive layer contains a colorant.

4. The dry film photoresist element described in claim 1 wherein the solid photosensitive layer contains an adhesion promoter.

5. The dry film photoresist element described in claim 1 wherein the solid photosensitive layer contains a surfactant.

6. The dry film photoresist element of claim 1 wherein said polymer is selected from a homopolymer, copolymer, terpolymer and block polymer.

7. The dry film photoresist element of claim 6 wherein said polymer comprises a copolymer of benzyl methacrylate and tetrahydropyranyl methacrylate.

8. The dry film photoresist element of claim 1 wherein an acid labile monomer used to form said polymer is selected from the group comprising:

1-ethoxyethyl methacrylate,
1-ethoxyethyl acrylate
1-butoxyethyl methacrylate,
1-butoxyethyl acrylate,
1-ethoxy-1-propyl methacrylate,
1-ethoxy-1-propyl acrylate,
tetrahydropyranyl methacrylate,
tetrahydropyranyl acrylate,
tetrahydropyranyl p-vinylbenzoate,
1-ethoxy-1-propyl-p-vinylbenzoate,
4-(2-tetrahydropyranyloxy)benzyl methacrylate,
4-(2-tetrahydropyranyloxy)benzyl acrylate,
4-(1-butoxyethoxy)benzyl methacrylate, and
4-(1-butoxyethoxy)benzyl acrylate.

9. The dry film photoresist element of claim 1 wherein a monomer used to form said copolymer, terpolymer or block polymer comprises tetrahydropyranyl methacrylate.

10. The photoresist element of claim 1 wherein said polymer comprises a homopolymer of 4-(2-tetrahydropyranyloxy)benzyl methacrylate.

11. The photoresist element of claim 1 wherein said polymer is selected from the group comprising an acrylic, a methacrylic, a vinyl, urethane or polyester polymer.

12. The photoresist element of claim 6 wherein the polymer contains one or more comonomers having no pendant acid labile groups.

13. The photoresist element of claim 12 wherein the comonomer having no pendant acid labile groups is selected from the group comprising: methyl methacrylate, butyl methacrylate, benzyl methacrylate, benzyl acrylate, styrene, 2-ethylhexyl methacrylate and cyclohexyl methacrylate.

14. The photoresist element of claim 13 wherein one of the monomers is benzyl methacrylate.

23

15. The photoresist element of claim 11 wherein said polymer is selected from the group consisting of polymethacrylates, polyacrylates and polystyrenes.

16. The photoresist element of claim 1 wherein said polymer is prepared by group transfer polymerization.

17. The photoresist element of claim 1 wherein said polymer is prepared by free radical polymerization.

18. The photoresist element of claim 1 wherein the initiator system that generates acid upon exposure to actinic radiation is selected from the group comprising diazonium, phosphonium, sulfonium, iodonium salts, halogen compounds, organometal/organohalogen combinations, benzoin esters and o-nitrobenzyl esters of strong acids, and N-hydroxyamide and N-hydroxyimide sulfonates, and aryl naphthoquinonediazide-4-sulfonates.

19. The photoresist element of claim 18 wherein the acid generator comprises diphenyliodonium tosylate.

24

20. The photoresist of claim 1 wherein the acid generator is 3-(9-anthracenyl)propyldiphenylsulfonium hexafluoroantimonate.

21. The photoresist element of claim 1 wherein the acid generator is benzoin tosylate.

22. The photoresist element of claim 1 wherein the acid generator is triarylsulfonium hexafluoroantimonate.

23. The photoresist element of claim 18 wherein the initiator system contains at least one sensitizer.

24. The photoresist element of claim 18 wherein the acid generator comprises about 0.1% to about 10% by weight of the photoresist composition.

25. The photoresist element of claim 24 wherein the acid generator in the composition comprises about 0.5% to about 6% by weight.

26. The photoresist element of claim 1 wherein the T_g of the resist composition is adjusted so that the composition flows at a lamination temperature of about 100° C. to 110° C.

27. The photoresist of claim 26 wherein the T_g is 15° C. to 60° C.

* * * * *

25

30

35

40

45

50

55

60

65



US005939242A

United States Patent [19]

Tang et al.

[11] **Patent Number:** **5,939,242**[45] **Date of Patent:** **Aug. 17, 1999**

[54] **POSITIVE PHOTORESIST WITH AN ALKOXYALKYL ESTER GROUP-CONTAINING (CO)POLYMER AND CARBOXYL-GROUP CONTAINING (CO) POLYMER**

[75] **Inventors:** Qian Tang, Oberwil; Martin Roth, Hölstein, both of Switzerland

[73] **Assignee:** Ciba Specialty Chemicals Corporation, Tarrytown, N.Y.

[21] **Appl. No.:** 08/757,391

[22] **Filed:** Nov. 27, 1996

Related U.S. Application Data

[63] Continuation-in-part of application No. 08/476,915, Jun. 7, 1995, abandoned.

[51] **Int. Cl.⁶** G03C 5/16; G03C 1/73

[52] **U.S. Cl.** 430/329; 430/323; 430/270.1; 430/326; 430/910

[58] **Field of Search** 430/270.1, 326, 430/910, 323, 329

[56] **References Cited****U.S. PATENT DOCUMENTS**

| | | | |
|-----------|---------|-----------------|---------|
| 5,120,633 | 6/1992 | Bauer et al. | 430/270 |
| 5,252,427 | 10/1993 | Bauer et al. | 430/270 |
| 5,262,281 | 11/1993 | Bauer et al. | 430/323 |
| 5,369,200 | 11/1994 | Schadeli et al. | 526/262 |
| 5,397,680 | 3/1995 | Schadeli et al. | 430/270 |
| 5,482,816 | 1/1996 | Murata et al. | 430/910 |

FOREIGN PATENT DOCUMENTS

| | | | |
|---------|---------|--------------------|------------|
| 0451741 | 10/1991 | European Pat. Off. | G03F 7/039 |
|---------|---------|--------------------|------------|

| | | | |
|---------|---------|--------------------|-------------|
| 0454334 | 10/1991 | European Pat. Off. | G03F 7/039 |
| 0488525 | 6/1992 | European Pat. Off. | G03F 7/004 |
| 0558280 | 9/1993 | European Pat. Off. | G03F 7/004 |
| 0568827 | 11/1993 | European Pat. Off. | G03F 7/16 |
| 0601974 | 6/1994 | European Pat. Off. | C08F 222/40 |
| 2248952 | 10/1990 | Japan | G03F 7/022 |
| 4-26850 | 1/1992 | Japan | G03F 7/039 |
| 517711 | 7/1993 | Japan | C09D 7/039 |

OTHER PUBLICATIONS

English Translation of JP 4-26850 Mayashi et al, Jan. 30, 1992.

Patent Abstracts of Japan, vol. 17, No. 291 JP 5017711, Jan. 1993.

Primary Examiner—Bernard Codd

Attorney, Agent, or Firm—David R. Crichton; Jacob M. Levine

[57] **ABSTRACT**

Positive photoresist compositions which can be developed in aqueous-alkaline media, comprising

(a) at least one homopolymer or copolymer containing acid-labile α -alkoxyalkyl ester groups,

(b) at least one carboxyl-containing copolymer in which the content of carboxyl groups is from 0.40 to 5.50 mol/kg,

(c) at least one compound which forms an acid on exposure to actinic radiation, and

(d) an organic solvent,

have high photosensitivity, a long shelf life of the components and of coatings produced therefrom and are particularly suitable as etch resists for the production of printed circuits.

14 Claims, No Drawings

**POSITIVE PHOTORESIST WITH AN
ALKOXYALKYL ESTER GROUP-
CONTAINING (CO)POLYMER AND
CARBOXYL-GROUP CONTAINING (CO)
POLYMER**

This application is a continuation-in-part of Ser. No. 08/476,915, filed Jun. 7, 1995, now abandoned.

The present invention relates to a positive photoresist composition which can be developed in aqueous-alkaline media, and to a process for the production of relief structures using this photoresist composition.

The lithographic production of relief structures on diverse substrates is frequently carried out using etch resists which contain a binder containing acid-sensitive groups and an acid photogenerator.

JP Kokai Hei 02-248952 describes photoresist compositions based on phenolic resins all or some of whose hydroxyl groups are substituted by tetrahydropyranyl ether groups. These compositions are distinguished by a high resolution capacity. However, they have the disadvantage of requiring heat treatment after exposure.

JP Kokai Hei 05-17711 discloses an etch resist composition comprising a copolymer of (meth)acrylic acid, tetrahydropyranyl (meth)acrylate and an alkyl acrylate and an acid photogenerator. This composition is deposited on the substrate by electrodeposition coating, giving a film of high homogeneity. However, the photosensitivity of this resist is relatively low. In addition, this process also requires heat treatment after exposure.

U.S. Pat. No. 5,252,427 describes copolymers which contain both acid-sensitive groups and free acid groups and which can be used in combination with conventional acid photogenerators as etch resists. However, the thermal stability of both the copolymers and the coatings produced therefrom is inadequate for certain applications.

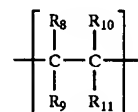
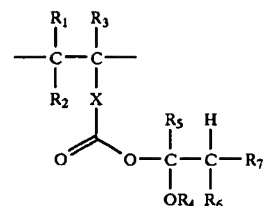
The mixtures of copolymers containing acid-sensitive groups and copolymers containing free acid groups which are described in EP-A 568 827 can also be employed in combination with conventional acid photogenerators as base resins for positive photoresists. These photoresists again have the disadvantage of relatively low photosensitivity and of requiring heat treatment after irradiation.

It has now been found that the use of mixtures of specific organic homopolymers or copolymers gives photoresist materials of high photosensitivity which do not require thermal aftertreatment, have a long shelf life and give relief structures of good resolution.

The present invention relates to a positive photoresist composition which can be developed in aqueous-alkaline media, comprising

- (a) at least one homopolymer or copolymer containing acid-labile α -alkoxyalkyl ester groups,
- (b) at least one carboxyl-containing copolymer in which the content of carboxyl groups is from 0.40 to 5.50 mol/kg,
- (c) at least one compound which forms an acid on exposure to actinic radiation, and
- (d) an organic solvent.

Component (a) is preferably a homopolymer or copolymer comprising 8–100% by weight of recurring structural units of the formula 1a and 92–0% by weight of recurring structural units of the formula 1b



in which

X is a direct bond or a divalent organic group having 1–18 carbon atoms, in which one or more carbon atoms may be replaced by oxygen, sulfur or non-basic nitrogen atoms,

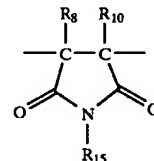
R_1 , R_2 and R_3 , independently of one another are hydrogen, C_1 – C_6 alkyl, C_5 – C_{14} aryl, C_6 – C_{20} aralkyl, halogen, $-\text{COOH}$, $-\text{COOR}_{12}$ or $-\text{CONR}_{13}\text{R}_{14}$, where R_{12} is an unsubstituted or C_1 – C_6 alkoxy-, hydroxyl- or halogen-substituted C_1 – C_{18} alkyl group or the radical of a hydroxyl-terminated polyether or polyester, and R_{13} and R_{14} , independently of one another, are hydrogen, C_1 – C_{18} alkyl, C_5 – C_{14} aryl or C_6 – C_{20} aralkyl,

R_4 is C_1 – C_6 alkyl or phenyl,

R_5 is hydrogen or C_1 – C_6 alkyl, and

R_6 and R_7 , independently of one another, are hydrogen, C_1 – C_6 alkyl or C_1 – C_6 alkoxy, or two of the radicals R_4 , R_5 , R_6 or R_7 , together with the carbon or oxygen atoms to which they are bonded, form a 5- to 8-membered ring,

R_8 , R_9 , R_{10} and R_{11} , independently of one another, are hydrogen, C_1 – C_{18} alkyl, unsubstituted or C_1 – C_6 alkyl-, C_1 – C_6 alkoxy- or halogen-substituted phenyl, halogen, C_1 – C_{18} alkoxy, $-\text{COOR}_{12}$, $-\text{OCOR}_{12}$ or $-\text{COOH}$, in which R_{12} is as defined above, or R_9 and R_{11} together with the carbon atoms to which they are bonded, form a five-membered ring having the structure



in which R_{15} is hydrogen, C_1 – C_{18} alkyl, C_5 – C_{14} aryl, C_6 – C_{20} aralkyl or hydroxyl-, alkoxy- or halogen-substituted phenyl,

with the proviso that the mean molecular weight (weight average) of the homopolymer or copolymer is 1000–500,000 and the amount of COOH groups is at most 0.4 mol/kg.

The divalent radical X can be any divalent aliphatic, cycloaliphatic, aromatic, araliphatic or heterocyclic radical having 1–18 carbon atoms and may, if desired, contain hetero atoms, such as O, N or S, or functional groups, such as carbonyl groups or ester groups.

3

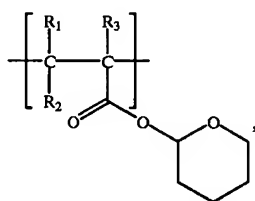
The term non-basic nitrogen atoms is taken to mean quaternized nitrogen atoms or nitrogen atoms containing electronegative substituents, for example carbonyl groups.

Alkyl or alkoxy groups R_1 to R_{12} or alkyl or alkoxy groups as substituents of phenyl groups may be straight-chain or branched. Examples which may be mentioned are: methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, 2-ethylhexyl, methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy, tert-butoxy, n-pentoxy, neopentoxy and n-hexoxy.

Halogen atoms as substituents are preferably bromine or chlorine atoms.

In the formula Ia, R_1 and R_2 are preferably hydrogen, and R_3 is hydrogen or methyl.

Component (a) is particularly preferably a homopolymer or copolymer comprising recurring structural units of the formula III



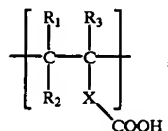
(III)

in which

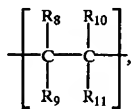
R_1 , R_2 and R_3 , independently of one another, are hydrogen, C_1 - C_6 alkyl, phenyl or halogen.

Component (a) is especially preferably a homopolymer or copolymer comprising recurring structural units of the formula III in which R_1 and R_2 are hydrogen and R_3 is hydrogen or methyl.

Component (b) is preferably a homopolymer or copolymer comprising 5-40% by weight of recurring structural units of the formula IIa and 95-60% by weight of recurring structural units of the formula IIb



(IIa)



(IIb)

in which

X is a direct bond or a divalent organic group having 1-18 carbon atoms, in which one or more carbon atoms may be replaced by oxygen, sulfur or non-basic nitrogen atoms,

R_1 , R_2 and R_3 , independently of one another are hydrogen, C_1 - C_6 alkyl, C_5 - C_{14} aryl, C_6 - C_{20} aralkyl, halogen, $-\text{COOH}$, $-\text{COOR}_{12}$ or $-\text{CONR}_{13}\text{R}_{14}$, where R_{12} is an unsubstituted or C_1 - C_6 alkoxy-, hydroxyl- or halogen-substituted C_1 - C_{18} alkyl group or the radical of a hydroxyl-terminated polyether or polyester, and R_{13} and R_{14} , independently of one another, are hydrogen, C_1 - C_{18} alkyl, C_5 - C_{14} aryl or C_6 - C_{20} aralkyl,

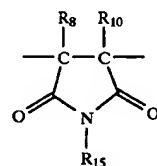
4

R_4 is C_1 - C_6 alkyl or phenyl,

R_5 is hydrogen or C_1 - C_6 alkyl, and

R_6 and R_7 , independently of one another, are hydrogen, C_1 - C_6 alkyl or C_1 - C_6 alkoxy, or two of the radicals R_4 , R_5 , R_6 or R_7 , together with the carbon or oxygen atoms to which they are bonded, form a 5- to 8-membered ring,

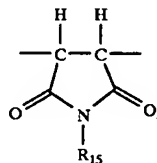
R_8 , R_9 , R_{10} and R_{11} , independently of one another, are hydrogen, C_1 - C_{18} alkyl, unsubstituted or C_1 - C_6 alkyl-, C_1 - C_6 alkoxy- or halogen-substituted phenyl, halogen, C_1 - C_{18} alkoxy, $-\text{COOR}_{12}$, $-\text{OCOR}_{12}$ or $-\text{COOH}$, in which R_{12} is as defined above, or R_9 and R_{11} together with the carbon atoms to which they are bonded, form a five-membered ring having the structure



in which R_{15} is hydrogen, C_1 - C_{18} alkyl, C_5 - C_{14} aryl, C_6 - C_{20} aralkyl or hydroxyl-, alkoxy- or halogen-substituted phenyl, with the proviso that the mean molecular weight (weight average) of the copolymer is 1000-500,000 daltons and the content of carboxyl groups is from 0.40 to 5.50 mol/kg, preferably from 0.45 to 4.00 mol/kg and in particular from 0.50 to 3.00 mol/kg.

Component (b) is preferably a homopolymer or copolymer comprising recurring structural units of the formula IIa in which R_1 and R_2 are hydrogen, R_3 is hydrogen or methyl, and X is a direct bond.

In the structural units of the formula IIb, R_8 and R_9 are preferably hydrogen, R_{10} is hydrogen or methyl, and R_{11} is preferably phenyl or $-\text{COOR}_{12}$, in which R_{12} is C_1 - C_{18} alkyl. Preference is furthermore given to copolymers comprising recurring structural units of the formula



in which R_{15} is phenyl.

Especially preferred components (b) contain 7-35% by weight, in particular 10-30% by weight, of recurring structural units of the formula IIa and 93-65% by weight, in particular 90-70% by weight, of recurring structural units of the formula IIb.

The homopolymers and copolymers of components (a) and (b) can be prepared in a known manner by anionic, cationic or group-transfer polymerization or in particular by free-radical polymerization on the corresponding unsaturated monomers.

The free-radical polymerization or copolymerization can be carried out using various methods. These have been described, for example, by S. Sandler and W. Karo in "Polymer Synthesis", Vol. 1, pp. 3-17, 1968, Academic Press, New York. Examples of conventional polymerization processes are bulk and solution polymerization, and furthermore emulsion, suspension and precipitation polymerization.

5

If desired, the molecular weight can be adjusted by adding small amounts of a regulator.

The polymerization is generally initiated by a conventional free-radical initiator. These include thermal initiators, such as azo compounds, for example α, α' -azoisobutyronitrile (AIBN), or peroxides, for example benzoyl peroxide, or redox initiator systems, such as the mixture of iron(III) acetylacetonate, benzoin and benzoyl peroxide, or photochemical free-radical formers, such as benzoin or benzil dimethyl ketal.

The polymerization is preferably carried out in solution. The reaction temperature is generally in the range from 10 to 200° C., preferably from 40 to 150° C., particularly preferably from 40 to 100° C.

Any solvent present must be inert under the reaction conditions. Examples of suitable solvents are aromatic hydrocarbons, chlorinated hydrocarbons, alcohols, ketones and ethers. Examples thereof are: benzene, toluene, xylenes, ethylbenzene, isopropylbenzene, ethylene chloride, propylene chloride, methylene chloride, chloroform, methyl ethyl ketone, acetone, methoxypropyl acetate, isopropanol, cyclohexanone, diethyl ether and tetrahydrofuran.

Examples of suitable monomers for the preparation of homopolymers or copolymers containing acid-labile α -alkoxyalkyl ester groups are 1-ethoxyethyl acrylate, methacrylate and p-vinylbenzoate, 1-butoxyethyl acrylate, methacrylate and p-vinylbenzoate, 1-ethoxy-1-propyl acrylate, methacrylate and p-vinylbenzoate, and tetrahydropyranloxy acrylate, methacrylate and p-vinylbenzoate.

Particular preference is given to tetrahydropyranlyl acrylate and methacrylate.

The monomers containing acid-labile α -alkoxyalkyl ester groups can be homopolymerized or alternatively copolymerized with one or more further monomers.

Examples of suitable monomers for the preparation of copolymers are ethylene, propylene, styrene, vinyl chloride, vinyl acetate, acrylic and methacrylic acid, methyl acrylate and methacrylate, ethyl acrylate and methacrylate, butyl acrylate and methacrylate, benzyl acrylate and methacrylate, 2-ethylhexyl acrylate and methacrylate and 2-hydroxyethyl acrylate and methacrylate.

Preference is given to methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate, benzyl methacrylate, 2-ethylhexyl methacrylate and 2-hydroxyethyl methacrylate.

The carboxyl-containing homopolymers and copolymers of component (b) can be prepared analogously by free-radical polymerization of the corresponding unsaturated carboxylic acids.

Examples of suitable carboxylic acids are maleic acid, itaconic acid, cinnamic acid, crotonic acid, p-vinylbenzoic acid and in particular acrylic acid and methacrylic acid.

The unsaturated carboxylic acids can be copolymerized with one or more further monomers, for example ethylene, propylene, styrene, vinyl chloride, vinyl acetate, methyl acrylate and methacrylate, ethyl acrylate and methacrylate, butyl acrylate and methacrylate, benzyl acrylate and methacrylate, 2-ethylhexyl acrylate and methacrylate, 2-hydroxyethyl acrylate and methacrylate and N-phenylmaleimide.

Preferred comonomers are methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate, benzyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-ethylhexyl methacrylate and N-phenylmaleimide.

Component (a) in preferred compositions according to the invention comprises at least one homopolymer or copolymer comprising 20–100% by weight, in particular 30–100% by

6

weight, of recurring structural units of the formula Ia and 80–0% by weight, in particular 70–0% by weight, of recurring structural units of the formula Ib.

Component (b) in the compositions according to the invention preferably comprises at least one copolymer comprising 5–35% by weight, in particular 10–30% by weight of recurring structural units of the formula IIa and 95–65% by weight, in particular 90–70% by weight, of recurring structural units of the formula IIb.

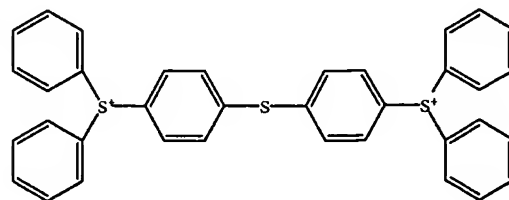
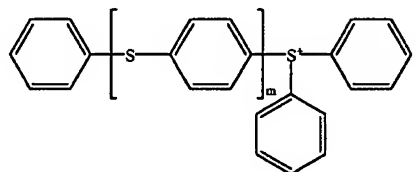
The mixing ratio between components (a) and (b) can vary within a broad range. The compositions according to the invention preferably comprise 10–95% by weight, in particular 20–80% by weight, of component (a) and 90–5% by weight, in particular 80–20% by weight, of component (b), based on the sum of components (a)+(b).

Component (c) can in principle be any compound which forms an acid on exposure to actinic radiation which is known to the skilled worker in resist technology, for example onium salts, disulfones, iron/arene complexes, compounds containing photolabile halogen atoms (for example halomethyltriazines, tetrabromomethane, etc), sulfonic acid esters, for example nitrobenzyl sulfonate, oxime sulfonates, α -sulfonyloxyketones, N-hydroxyimidosulfonates and N-hydroxyarnidosulfonates.

Examples of suitable photoinitiators are described in EP-A 451 741 and EP-A 568 827.

Component (c) is preferably a photosensitive diazonium, sulfonium, sulfoxonium or iodonium salt or a photosensitive sulfonic acid ester.

Component (c) is particularly preferably triphenylsulfonium trifluoromethanesulfonate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium hexafluorophosphate, triphenylsulfonium hexafluoroantimonate or a hexafluorophosphate or hexafluoroantimonate of the following sulfonium ions:



in which m is an integer from 1 to 10.

Component (c) is generally employed in an amount of from 1–20% by weight, preferably 2–10% by weight, based on the sum of components (a)+(b).

If expedient, sensitizers can be added to the compositions according to the invention. These sensitizers increase the spectral sensitivity of the photoinitiator system at the desired wavelength. The choice of suitable sensitizer depends essentially on the photoinitiator selected. For example, sulfonium and iodonium salts only have adequate photosensitivity at wavelengths of <350 nm. The sensitivity of such compounds at higher wavelengths can be significantly increased, for example, by adding aromatic hydrocarbons, such as perylene, pyrene, anthracene and derivatives thereof, phe-

nothiazine or phenothiazine derivatives, or unsubstituted or substituted thioxanthone. The aminoaryl ketones disclosed, for example, in U.S. Pat. No. 4,755,450 are also suitable as sensitizers for sulfonium and iodonium salts. Other suitable sensitizers are the arylidene aryl ketones disclosed in U.S. Pat. No. 4,162,162.

The compositions according to the invention can include further conventional additives, for example stabilizers, pigments, dyes, fillers, adhesion promoters, flow-control agents, wetting agents and plasticizers.

In order to increase the shelf life, it may be expedient to add small amounts of weakly basic additives to the compositions according to the invention. Examples of suitable basic compounds are primary, secondary and tertiary aliphatic, cycloaliphatic and aromatic amines and N-heterocyclic compounds. Examples which may be mentioned are: triethylamine, tripropylamine, tributylamine, aniline, N-methylaniline, N,N-dimethylaniline, 1-naphthylamine, 2-naphthylamine, diphenylamine, ethylenediamine, hexamethylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 4,4'-diaminobenzophenone, 4,4'-diaminodiphenylamine, pyrrolidine and derivatives thereof, piperidine and derivatives thereof, imidazole and derivatives thereof, for example 4-methylimidazole, 4-methyl-2-phenylimidazole, 4,5-diphenylimidazole and in particular 1-methylimidazole.

The amount in which the basic additives are expediently added depends essentially on the amount of acid photogenerator (c), and is preferably 0.01–5.0 mmol, in particular 0.02–2.0 mmol, of basic additive per gram of acid photogenerator.

A stabilizing action is also achieved if the polymers of components (a) and/or (b) contain small amounts of basic substituents, for example amino groups. In order to prepare such polymers, a small amount of unsaturated monomers containing basic substituents is added to the unsaturated starting monomers during the free-radical polymerization. Examples of suitable monomers containing basic substituents are amino-substituted acrylates, such as 2-dimethylaminoethyl acrylate, 2-dimethylaminoethyl methacrylate, 2-diethylaminoethyl acrylate, 2-diethylaminoethyl methacrylate, dimethylaminopropylacrylamide, dimethylaminopropylmethacrylamide, 2-t-butylaminoethyl acrylate and 2-t-butylaminoethyl methacrylate, and vinylpyridines, such as 2-vinylpyridine or 4-vinylpyridine.

The amount in which such comonomers containing basic substituents are expediently employed depends essentially on the amount of acid photogenerator (c) and is preferably 0.01–5.0 mmol, in particular 0.02–2.0 mmol, of comonomer containing basic substituents per gram of acid photogenerator.

The choice of solvent and concentration depends principally on the composition type and on the coating method. The solvent must be inert, i.e. it must not undergo any chemical reaction with the components and it must be removable again during drying after coating. Examples of suitable solvents are ketones, ethers and esters, such as methyl ethyl ketone, 2-heptanone, cyclopentanone, cyclohexanone, γ -butyrolactone, ethyl pyruvate, diethylene glycol dimethyl ether, 2-methoxyethanol, 2-ethoxyethanol, 2-ethoxyethyl acetate, 1-methoxy-2-propyl acetate, 1,2-dimethoxyethane, ethyl acetate and 3-methoxymethyl propionate.

The preferred solvent is methoxypropyl acetate.

The solids content of the compositions depends on the application method and on the desired coating thickness and is typically from 10 to 80% by weight.

The solution is applied uniformly to a substrate by known coating methods, for example by spincoating, dipping, knife coating, curtain coating, brushing, spraying and especially by electrostatic spraying and reverse-roll coating. It is also possible to apply the photosensitive coating to a temporary, flexible support and then to coat the final substrate, for example a copper-laminated circuitboard, by transferring the coating by lamination.

The application rate (coating thickness) and the substrate type (coating support) depend on the desired area of application. The coating thickness range generally covers values of about 1 μm to about 20 μm , preferably 3–15 μm .

After the coating, the solvent is generally removed by drying preferably at temperatures of from 20° C. to 100° C., giving a coating of the composition according to the invention on the substrate.

In order to produce relief structures, the substrate coated with the composition according to the invention is exposed imagewise to actinic radiation. The term "actinic radiation" is generally taken to mean UV or VIS radiation, preferably in the wavelength range of 220–550 nm. The term "image-wise" exposure covers both exposure through a photomask containing a predetermined pattern and exposure by a laser beam, which is moved, for example, under computer control, over the surface of the coated substrate.

Radiation sources which can be used are in principle all lamps which emit radiation in the UV and/or VIS region. Both point light sources and spread emitters (lamp carpets) are suitable. Examples are: carbon arc lamps, xenon arc lamps, mercury vapour lamps, if desired doped with metal halides (metal halide lamps), fluorescent lamps, argon incandescent lamps, electronic flash lamps, photographic flood lamps, electron beams and X-rays. The distance between the lamp and the novel image material can vary depending on the application and lamp type and strength, for example between 2 cm and 150 cm. Particularly suitable are laser light sources, for example argon ion lasers and krypton ion lasers. Laser light also allows the resist to be exposed without a mask by writing the controlled laser beam directly on the resist layer. The high sensitivity of the novel materials is very advantageous here, allowing high writing speeds at relatively low intensity. This method allows the production of printed circuits in the electronics industry, lithographic offset printing plates or relief printing plates and photographic image-recording materials.

In contrast to many known positive photoresist systems based on chemical amplification, there is surprisingly no need when using the compositions according to the invention to subject the resist to heat treatment after exposure, known as "post exposure bake", in order to ensure complete reaction of the acid-sensitive groups in the polymer structure with the acid generated by the exposure and to remove volatile reaction products.

If desired, however, such heat treatment can be carried out without adverse consequences for the exposed structures.

After the material has been exposed imagewise in the conventional manner, the exposed areas of the photoresist are removed by dissolution in a developer.

The choice of the particular developer depends on the type of photoresist, in particular on the nature of the binder used or the photolysis products formed. The developer can comprise aqueous solutions of bases to which organic solvents or mixtures thereof may have been added.

Particularly preferred developers are aqueous-alkaline solutions, as also employed for the development of naphthoquinone diazide coatings. These include, in particular, aqueous solutions of alkali metal silicates, phosphates,

hydroxides and carbonates. If desired, relatively small amounts of wetting agents and/or organic solvents can also have been added to these solutions.

Examples of typical organic solvents which may be added to the developer fluids are cyclohexanone, 2-ethoxyethanol, acetone, isopropanol, ethanol and mixtures of two or more of these solvents.

The radiation-sensitive compositions according to the invention are suitable as photoresists for electronics, in particular as etch resists for the production of printed circuits or as microresists for the production of integrated circuits, and for the production of printing plates, for example offset printing plates.

In the preferred use of the composition according to the invention, as etch resists, the metal uncovered by the development, usually copper, can be removed using any known etchant, for example solutions of iron chloride, hydrogen peroxide/phosphoric acid, ammonium persulfate or copper chloride.

The photoresist coating which remains can subsequently be removed by stripping with strong aqueous bases, for example NaOH or KOH, and/or organic solvents.

The present invention thus furthermore relates a process for the production of relief structures on a circuit board, which comprises coating a substrate with a composition according to claim 1 and exposing the film obtained after removal of the solvent imagewise and subsequently developing the exposed film in an aqueous-alkaline medium.

A preferred embodiment of the invention is a process for the production of relief structures which comprises the following steps:

- (A) coating a copper-laminated substrate with a composition according to claim 1 by application of liquid resists by known methods;
- (B) removal of the solvent by drying at temperatures of from 30° C. to 130° C.;
- (C) exposure to actinic radiation through a mask or by means of direct laser irradiation;
- (D) development using aqueous-alkaline or semiaqueous-alkaline developer solutions;
- (E) etching with acidic or weakly alkaline etchants;
- (F) removal of the photoresist coating which remains by stripping with strong aqueous bases and/or organic solvents.

Particular mention should be made of the extremely good thermal stability of the individual components and the resultant coatings on storage.

A suitable choice of the polymers of components (a) and (b) also allows the mechanical properties of the resist composition to be varied within a broad range. For example, use of hard polymers allows very high mechanical strength to be achieved.

EXAMPLES

I. Preparation of the Polymers

I.1. Poly-2-tetrahydropyranyl methacrylate

A solution of 10 g (59 mmol) of 2-tetrahydropyranyl methacrylate and 0.25 g of azoisobutyronitrile (AIBN) in 15 g of methoxypropyl acetate is stirred for 8 hours at 80° C. under a nitrogen atmosphere. The resultant solution of poly-2-tetrahydropyranyl methacrylate ($M_n=4435$, $M_w=91,593$) can be further processed directly (without isolation of the polymer).

Acid content of the solution: 0.033 mol/kg; Acid content after 9 months at room temperature: 0.040 mol/kg.

I.2. Copolymer of 2-tetrahydropyranyl methacrylate, methyl methacrylate and 2-ethylhexyl methacrylate

Analogously to Example I.1, a solution of 25.2 g (148 mmol) of 2-tetrahydropyranyl methacrylate, 10.4 g (104 mmol) of methyl methacrylate, 4.4 g (22 mmol) of 2-ethylhexyl methacrylate and 1 g of azoisobutyronitrile in 60 g of methoxypropyl acetate is stirred for 8 hours under nitrogen. The resultant solution of the copolymer ($M_n=7237$, $M_w=48,154$) can be further processed directly.

I.3. Copolymer of 2-tetrahydropyranyl methacrylate, methyl methacrylate and 2-hydroxyethyl methacrylate

A solution of 56.7 g (333 mmol) of 2-tetrahydropyranyl methacrylate, 23.4 g (234 mmol) of methyl methacrylate, 9.9 g (76 mmol) of 2-hydroxyethyl methacrylate and 2 g of azoisobutyronitrile in 50 g of methoxypropyl acetate is added dropwise over the course of one hour with stirring at 80° C. under nitrogen to a mixture of 6.3 g (37 mmol) of 2-tetrahydropyranyl methacrylate, 2.6 g (26 mmol) of methyl methacrylate, 1.1 g (9 mmol) of 2-hydroxyethyl methacrylate and 100 g of methoxypropyl acetate. Stirring is continued at 80° C., and, one hour after the addition, a further 0.5 g of azoisobutyronitrile is added. The solution is subsequently stirred at 80° C. for 6 hours. The resultant solution of the copolymer ($M_n=8103$, $M_w=47,096$) can be further processed directly.

I.4. Copolymer of 2-tetrahydropyranyl acrylate and methyl methacrylate

A solution of 34.02 g (218 mmol) of 2-tetrahydropyranyl acrylate, 19.98 g (200 mmol) of methyl methacrylate and 1.2 g of azoisobutyronitrile in 30 g of methoxypropyl acetate is added dropwise over the course of 1.5 hours with stirring at 80° C. under nitrogen to a mixture of 3.78 g (24 mmol) of 2-tetrahydropyranyl acrylate, 2.22 g (22 mmol) of methyl methacrylate and 60 g of methoxypropyl acetate. Stirring is continued at 80° C., and, one hour after the addition, a further 0.3 g of azoisobutyronitrile is added. The solution is subsequently stirred at 80° C. for a further 5.5 hours. The resultant solution of the copolymer ($M_n=8108$, $M_w=32,167$) can be further processed directly.

I.5. Copolymer of methacrylic acid, methyl methacrylate and 2-ethylhexyl methacrylate

Analogously to Example I.1., a solution of 4.0 g (47 mmol) of methacrylic acid, 12.0 g (120 mmol) of methyl methacrylate and 4.0 g (20 mmol) of 2-ethylhexyl methacrylate and 0.5 g of azoisobutyronitrile in 30 g of isopropanol is stirred for 8 hours under nitrogen. The resultant solution of the copolymer ($M_n=8691$, $M_w=54,540$, acid content=1.13 mol/kg) can be further processed directly.

I.6. Copolymer of methacrylic acid, methyl methacrylate and tert-butyl acrylate

A solution of 135 g (1.568 mol) of methacrylic acid, 630 g (6.30 mol) of methyl methacrylate, 135 g (1.05 mol) of tert-butyl acrylate and 12.5 g of azoisobutyronitrile in 500 g of isopropanol is added dropwise over the course of 2 hours with stirring at 80° C. under nitrogen to a mixture of 15.0 g (174 mmol) of methacrylic acid, 70 g (700 mmol) of methyl methacrylate, 15.0 g (117 mmol) of tert-butyl acrylate and 1000 g of isopropanol. Stirring is continued at 80° C., and, one hour after the addition, a further 2.5 g of azoisobutyronitrile are added.

The solution is subsequently stirred at 80° C. for a further 5 hours. The resultant solution of the copolymer ($M_n=8880$, $M_w=27,422$, acid content=0.75 mol/kg) can be further processed directly.

I.7. Copolymer of 2-tetrahydropyranyl methacrylate, methyl acrylate and 2-hydroxyethyl methacrylate

A solution of 34.02 g (200 mmol) of 2-tetrahydropyranyl methacrylate, 14.04 g (163 mmol) of methyl acrylate, 5.94 g (46 mmol) of 2-hydroxyethyl methacrylate and 1.74 g of

azoisobutyronitrile in 30 g of methoxypropyl acetate is added dropwise over the course of 6 hours with stirring at 70° C. under nitrogen to a mixture of 3.78 g (22 mmol) of 2-tetrahydropyranyl methacrylate, 1.56 g (18 mmol) of methyl acrylate, 0.66 g (5 mmol) of 2-hydroxyethyl methacrylate and 60 g of methoxypropyl acetate. Stirring is continued at 70° C., and, one hour after the addition, a further 0.18 g of azoisobutyronitrile is added. The solution is subsequently stirred at 70° C. for a further hour. The resultant solution of the copolymer ($M_n=9074$, $M_w=44,877$) can be further processed directly.

I.8. Copolymer of methacrylic acid, methyl methacrylate, ethyl acrylate and methacrylamide

A solution of 27 g (314 mmol) of methacrylic acid, 99 g (990 mmol) of methyl methacrylate, 45 g (450 mmol) of ethyl acrylate, 9.0 g (80 mmol) of methacrylamide and 2.5 g of azoisobutyronitrile in 100 g of methoxypropyl acetate is added dropwise over the course of 2.25 hours with stirring at 80° C. under nitrogen to a mixture of 3.0 g (35 mmol) of methacrylic acid, 11 g (110 mmol) of methyl methacrylate, 5.0 g (50 mmol) of ethyl acrylate, 1.0 g (9 mmol) of methacrylamide and 200 g of methoxypropyl acetate. Stirring is continued at 80° C., and, one hour after the addition, a further 0.5 g of azoisobutyronitrile is added.

The solution is subsequently stirred at 80° C. for a further 4.75 hours. The resultant solution of the copolymer ($M_n=8547$, $M_w=31,820$, acid content=0.84 mol/kg) can be further processed directly.

I.9. Copolymer of methacrylic acid, methyl methacrylate and ethyl acrylate

A solution of 27 g (314 mmol) of methacrylic acid, 99 g (990 mmol) of methyl methacrylate, 54 g (540 mmol) of ethyl acrylate and 2.5 g of azoisobutyronitrile in 100 g of methoxypropyl acetate is added dropwise over the course of 2 hours with stirring at 80° C. under nitrogen to a mixture of 3.0 g (35 mmol) of methacrylic acid, 11 g (110 mmol) of methyl methacrylate, 6.0 g (60 mmol) of ethyl acrylate and 200 g of methoxypropyl acetate. Stirring is continued at 80° C., and, one hour after the addition, a further 0.5 g of azoisobutyronitrile is added.

The solution is subsequently stirred at 80° C. for a further 5 hours. The resultant solution of the copolymer ($M_n=8993$, $M_w=43,314$, acid content=0.7 mol/kg) can be further processed directly.

I.10 Copolymer of methacrylic acid, methyl methacrylate and ethyl acrylate

A solution of 21.6 g (251 mmol) of methacrylic acid, 104.4 g (1.04 mol) of methyl methacrylate, 54 g (540 mmol) of ethyl acrylate and 4.0 g of azoisobutyronitrile in 100 g of methoxypropyl acetate is added dropwise over the course of 2 hours with stirring at 80° C. under nitrogen to a mixture of 2.4 g (28 mmol) of methacrylic acid, 11.6 g (116 mmol) of methyl methacrylate, 6.0 g (60 mmol) of ethyl acrylate and 200 g of methoxypropyl acetate. Stirring is continued at 80° C., and, one hour after the addition, a further 1.0 g of azoisobutyronitrile is added.

The solution is subsequently stirred at 80° C. for a further 5 hours. The resultant solution of the copolymer ($M_n=9275$, $M_w=30,304$, acid content=0.61 mol/kg) can be further processed directly.

I.11. Copolymer of methacrylic acid, methyl methacrylate and N-phenylmaleimide

A solution of 36.0 g (419 mmol) of methacrylic acid, 126 g (1.26 mol) of methyl methacrylate, 18 g (104 mmol) of N-phenylmaleimide and 5.0 g of TrigonoX C (Akzo product) in 100 g of methoxypropyl acetate is added dropwise over the course of 2 hours with stirring at 135° C. under nitrogen

to a mixture of 4.0 g ((26.5 mmol) of methacrylic acid, 14.0 g (140 mmol) of methyl methacrylate, 2.0 g (11.6 mmol) of N-phenylmaleimide and 200 g of methoxypropyl acetate.

The solution is subsequently stirred at 135° C. for 6 hours. The resultant solution of the copolymer ($M_n=3883$, $M_w=10,041$, acid content=0.933 mol/kg) can be further processed directly.

I.12. Copolymer of 2-tetrahydropyranyl acrylate, methyl methacrylate and 2-dimethylaminoethyl methacrylate

A solution of 56.7 g (333 mmol) of 2-tetrahydropyranyl methacrylate, 33.0 g (33 mmol) of methyl methacrylate, 0.27 g (1.72 mmol) of 2-dimethylaminoethyl methacrylate and 2.0 g of azoisobutyronitrile in 50 g of methoxypropyl acetate is added dropwise over the course of 2 hours with stirring at 70° C. under nitrogen to a mixture of 6.3 g (37 mmol) of 2-tetrahydropyranyl methacrylate, 3.67 g (36.7 mmol) of methyl methacrylate, 0.03 g (0.19 mmol) of 2-dimethylaminoethyl methacrylate and 100 g of methoxypropyl acetate. Stirring is continued at 70° C., and, one hour after the addition, a further 0.5 g of azoisobutyronitrile is added.

The solution is subsequently stirred at 70° C. for a further 5 hours. The resultant solution of the copolymer ($M_n=9334$, $M_w=44,050$) can be further processed directly.

II. Use examples

II.1. Positive Etch Resist

A solution of 0.23 g of the photoinitiator Degacure® KI 85 (Degussa) and 0.04 g of 9-methylanthracene in 3 g of methoxypropyl acetate is added to a mixture of 2 g of the solution from Example I.1. and 3 g of the solution from Example I.6. The resultant resist solution is filtered and subsequently applied to a copper-laminated substrate (18 μ m of copper) by means of a K-bar coater (36 μ m). The coated substrate is dried for 10 minutes at room temperature and subsequently for 15 minutes at 80° C., giving a resist film with a thickness of 9 μ m. Exposure is carried by means of a PR 340 ORC printer, SMX 7000H lamp, using a 21 step Stouffer sensitivity guide as mask (see W. S. DeForest, "Photoresist", McGraw-Hill Book Co., N.Y., pp. 109 ff.). The exposed energy is 80 mJ/cm². After about 5 minutes, the exposed plate is developed for 120 seconds with a 1% aqueous Na₂CO₃ solution (30° C., spray pressure 2 bar). After etching with CuCl₂/HCl solution at 45° C., a relief image with the final imaged step being No. 4 is obtained. Structures of 50 μ m are well resolved.

The resist is subsequently removed by immersion in aqueous 5% NaOH solution at 30° C.

II.2. Positive Etch Resist

A solution of 0.23 g of the photoinitiator Degacure® KI 85 (Degussa) and 0.04 g of 9-methylanthracene in 3 g of methoxypropyl acetate is added to a mixture of 3.5 g of the solution from Example I.2 and 1.5 g of the solution from Example I.5. The coating, exposure, development and etching are carried out in the same way as in Example II.1. The exposure energy is 80 mJ/cm². The development time is 120 s at 22° C. and a spray pressure of 2 bar. A relief image with the final imaged step being No. 3 is obtained. Structures of 25 μ m are well resolved.

II.3. Positive Etch Resist

A solution of 0.23 g of the photoinitiator Degacure® KI 85 (Degussa) and 0.04 g of 9-methylanthracene in 3 g of methoxypropyl acetate is added to a mixture of 2.5 g of the solution from Example I.2 and 2.5 g of the solution from Example I.6. The coating, exposure, development and etching are carried out in the same manner as in Example II.1.

Exposure energy: 80 mJ/cm²; Development time: 120 s (30° C./spray pressure 2 bar); Final imaged step: No. 3; Resolution: 25 μ m.

II.4. Positive Etch Resist

A solution of 0.16 g of the photoinitiator Cyracure 6990 (Union Carbide) and 0.04 g of Quantacure ITX (Ocel Chemicals) in 1.83 g of methoxypropyl acetate is added to a mixture of 1.5 g of the solution from Example I.2 and 4.67 g of a 30% solution of Scripset 550 in methoxypropyl acetate. The coating, exposure, development and etching are carried out in the same manner as in Example II.1.

Exposure energy: 125 mJ/cm² Development time: 120 s (35° C./spray pressure 1 bar); Final imaged step: No. 1; Resolution: 25 μm

A comparative test with the solution from Example I.2 after storage for 9 months at room temperature shows no difference.

II.5. Positive Etch Resist

A solution of 0.16 g of the photoinitiator Cyracure 6990 (Union Carbide), 0.04 g of Quantacure ITX (Ocel Chemicals) and 0.01 g of Orasolblau GN (Ciba) in 3 g of methoxypropyl acetate is added to a mixture of 3.0 g of the solution from Example I.3 and 2.0 g of the solution from Example I.5. The coating, exposure, development and etching are carried out in the same manner as in Example II.1.

Exposure energy: 150 mJ/cm² Development time: 100 s (30° C./spray pressure 1 bar) Final imaged step: Nr. 2 Resolution: 25 μm

II.6. Positive Etch Resist

A solution of 0.16 g of the photoinitiator Cyracure 6990 (Union Carbide) and 0.04 g of Quantacure ITX (Ocel Chemicals) in 2.17 g of methoxypropyl acetate is added to a mixture of 2.5 g of the solution from Example I.4 and 3.33 g of a 30% solution of Scripset 550 in methoxypropyl acetate. The coating, exposure, development and etching are carried out in the same manner as in Example II.1.

Exposure energy: 30 mJ/cm² Development time: 63 s (30° C./spray pressure 1 bar) Final imaged step: No. 3 Resolution: 25 μm

II.7. Positive Etch Resist

A solution of 0.32 g of the photoinitiator Cyracure 6974 (Union Carbide), 0.08 g of Quantacure ITX (Ocel Chemicals), 0.04 g of Pergascriptblau S-RB (Ciba), 0.02 g of triazine A ((PCAS) and 0.01 g of Orasolblau GN (Ciba) in 6 g of methoxypropyl acetate is added to a mixture of 7.0 g of the solution from Example I.3 and 3.0 g of the solution from Example I.8. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 114 mJ/cm² Development time: 70 s (30° C./spray pressure 1 bar) Final imaged step: No. 2 Resolution: 25 μm

II.8. Positive Etch Resist

A solution of 3.2 g of the photoinitiator Cyracure 6974 (Union Carbide), 0.8 g of Quantacure ITX (Ocel Chemicals), 0.4 g of Pergascriptblau S-RB (Ciba), 0.2 g of triazine A ((PCAS) and 0.1 g of Orasolblau GN (Ciba) in 22.7 g of methoxypropyl acetate is added to a mixture of 50 g of the solution from Example I.3 and 50 g of the solution from Example I.9. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a 64 g roller coater is used for the coating and a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 114 mJ/cm² Development time: 80 s (30° C./spray pressure 1 bar) Final imaged step: No. 3 Resolution: 25 μm

II.9. Positive Etch Resist

A solution of 0.32 g of the photoinitiator Cyracure 6974 (Union Carbide), 0.08 g of Quantacure ITX (Ocel

Chemicals), 0.04 g of Pergascriptblau S-RB (Ciba), 0.02 g of triazine A ((PCAS) and 0.01 g of Orasolblau GN (Ciba) in 6 g of methoxypropyl acetate is added to a mixture of 3.0 g of the solution from Example I.3 and 7.0 g of the solution from Example I.10. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 114 mJ/cm² Development time: 70 s (30° C./spray pressure 1 bar) Final imaged step: No. 1 Resolution: 25 μm

II.10. Positive Etch Resist

A solution of 0.32 g of the photoinitiator Cyracure 6974 (Union Carbide), 0.08 g of Quantacure ITX (Ocel Chemicals), 0.04 g of Pergascriptblau S-RB (Ciba), 0.02 g of triazine A ((PCAS) and 0.01 g of Orasolblau GN (Ciba) in 6 g of methoxypropyl acetate is added to a mixture of 5.0 g of the solution from Example I.7 and 5.0 g of the solution from Example I.10. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 130 mJ/cm² Development time: 70 s (30° C./spray pressure 1 bar) Final imaged step: No. 4 Resolution: 25 μm

II.11. Positive Etch Resist

A solution of 0.32 g of the photoinitiator Cyracure 6974 (Union Carbide), 0.08 g of Quantacure ITX (Ocel Chemicals), 0.09 g of Multiflow (Monsanto) and 0.01 g of Orasolblau GN (Ciba) in 5.7 g of methoxypropyl acetate is added to a mixture of 5.0 g of the solution from Example I.4 and 5.0 g of the solution from Example I.11. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 130 mJ/cm² Development time: 100 s (25° C./spray pressure 1 bar) Final imaged step: No. 4 Resolution: 25 μm

II.12. Positive Etch Resist

A solution of 0.32 g of the photoinitiator Cyracure 6974 (Union Carbide), 0.08 g of Quantacure ITX (Ocel Chemicals), 0.09 g of Multiflow (Monsanto), 0.63 mg of N-methylimidazole and 0.01 g of Orasolblau GN (Ciba) in 5.7 g of methoxypropyl acetate is added to a mixture of 5.0 g of the solution from Example I.4 and 5.0 g of the solution from Example I.11. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 200 mJ/cm² Development time: 40 s (30° C./spray pressure 1 bar) Final imaged step: No. 3 Resolution: 25 μm

II.13. Positive Etch Resist

A solution of 0.32 g of the photoinitiator Cyracure 6974 (Union Carbide), 0.08 g of Quantacure ITX (Ocel Chemicals), 0.09 g of Multiflow (Monsanto), 6.3 mg of N-methylimidazole and 0.01 g of Orasolblau GN (Ciba) in 5.7 g of methoxypropyl acetate is added to a mixture of 5.0 g of the solution from Example I.4 and 5.0 g of the solution from Example I.11. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 200 mJ/cm² Development time: 70 s (30° C./spray pressure 1 bar) Final imaged step: No. 3 Resolution: 25 μm

II.14. Positive Etch Resist

15

A solution of 0.32 g of the photoinitiator Cyracure 6974 (Union Carbide), 0.08 g of Quantacure ITX (Ocel Chemicals), 0.04 g of Pergascriptblau S-RB (Ciba), 0.2 g of triazine A ((PCAS) and 0.01 g of Orasolblau GN (Ciba) in 6 g of methoxypropyl acetate is added to a mixture of 4.0 g of the solution from Example I.7 and 6.0 g of the solution from Example I.11. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 130 mJ/cm² Development time: 60 s (30° C./spray pressure 1 bar) Final imaged step: No. 5 Resolution: 25 μm

II.15. Positive Etch Resist

A solution of 0.16 g of the photoinitiator (4-nitrophenyl) methyl 9,10dihydroxy-2-anthracenesulfonate, 0.4 g of Pergascriptblau S-RB (Ciba), 0.2 g of triazine A ((PCAS) and 0.01 g of Orasolblau GN (Ciba) in 5.7 g of methoxypropyl acetate is added to a mixture of 4.0 g of the solution from Example I.7 and 6.0 g of the solution from Example I.11. The coating, exposure, development and etching are carried out in the same manner as in Example I.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 130 mJ/cm² Development time: 70 s (30° C./spray pressure 1 bar) Final imaged step: No. 2 Resolution: 25 μm

II.16. Positive Etch Resist

A solution of 0.32 g of the photoinitiators Cyracure 6974 (Union Carbide), 0.08 g of Quantacure ITX (Ocel Chemicals), 0.09 g of Multiflow (Monsanto) and 0.01 g of Orasolblau GN (Ciba) in 5.7 g of methoxypropyl acetate is added to a mixture of 5.0 g of the solution from Example I.11 and 5.0 g of the solution from Example I.12. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

Exposure energy: 200 mJ/cm² Development time: 135 s (30° C./spray pressure 1 bar) Final imaged step: No. 2; Resolution: 25 μm

II.17. Positive Etch Resist

A solution of 0.16 g of the photoinitiator diphenyliodonium hexafluoroarsenate, 0.08 g of Quantacure ITX (Ocel Chemicals), 0.09 g of Multiflow (Monsanto) and 0.01 g of Orasolblau GN (Ciba) in 5.7 g of methoxypropyl acetate is added to a mixture of 5.0 g of the solution from Example I.11 and 5.0 g of the solution from Example I.12. The coating, exposure, development and etching are carried out in the same manner as in Example II.1, but a Staub LB 65-1/5000 W lamp is used for the exposure.

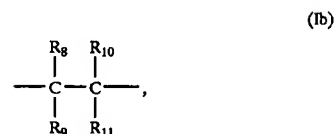
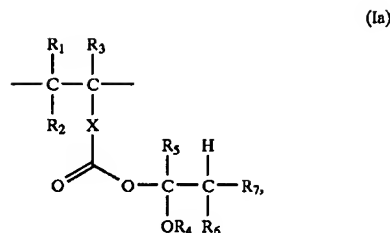
Exposure energy: 130 mJ/cm² Development time: 70 s (30° C./spray pressure 1 bar) Final imaged step: No. 5 Resolution: 25 μm

What is claimed is:

1. A positive photoresist composition which can be developed in aqueous-alkaline media, consisting essentially of

- (a) at least one a homopolymer or copolymer comprising 8–100% by weight of recurring structural units of the formula Ia and 92–0% by weight of recurring structural units of the formula Ib

16



in which

X is a direct bond or a divalent aliphatic, cycloaliphatic or heterocyclic radical having 1–18 carbon atoms, in which one or more carbon atoms may be replaced by oxygen, sulfur or non-basic nitrogen atoms,

R₁, R₂ and R₃, independently of one another are hydrogen, C₁–C₆alkyl, C₅–C₁₄aryl, C₆–C₂₀aralkyl, halogen, —COOH, —COOR₁₂ or —CONR₁₄, where R₁₂ is an unsubstituted or C₁–C₆alkoxy-, hydroxyl- or halogen-substituted C₁–C₁₈alkyl group or the radical of a hydroxyl-terminated polyether or polyester, and R₁₃ and R₁₄, independently of one another, are hydrogen, C₁–C₁₈alkyl, C₅–C₁₄aryl or C₆–C₂₀aralkyl,

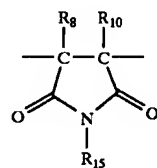
R₄ is C₁–C₆alkyl or phenyl,

R₅ is hydrogen or C₁–C₆alkyl, and

R₆ and R₇, independently of one another, are hydrogen, C₁–C₆alkyl or C₁–C₆alkoxy, or two of the radicals R₄, R₅, R₆ or R₇, together with the carbon or oxygen atoms to which they are bonded, form a 5- to 8-membered ring,

R₈, R₉, R₁₀ and R₁₁, independently of one another, are hydrogen, C₁–C₁₈alkyl, unsubstituted or C₁–C₆alkyl-, C₁–C₆alkoxy- or halogen-substituted phenyl, halogen, C₁–C₁₈alkoxy, —COOR₁₂, —OCOR₁₂ or —COOH, in which R₁₂ is as defined above,

or R₉ and R₁₁ together with the carbon atoms to which they are bonded, form a five-membered ring having the structure

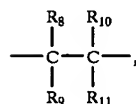
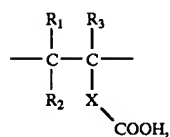


in which R₁₅ is hydrogen, C₁–C₁₈alkyl, C₅–C₁₄aryl, C₆–C₂₀aralkyl or hydroxyl-, alkoxy- or halogen-substituted phenyl,

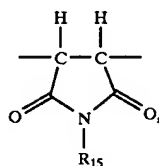
with the proviso that the mean molecular weight (weight average) of the homopolymer or copolymer is 1000–500,000 and the amount of COOH groups is at most 0.4 mol/kg,

- (b) at least one copolymer comprising 5–40% by weight of recurring structural units of the formula Ia and 95–60% by weight of recurring structural units of the formula Ib

17



in which R_1 , R_2 , R_3 and X are as defined in formulas Ia and Ib, in which R_8 and R_9 are hydrogen, R_{10} is hydrogen or methyl and R_{11} is phenyl or $-\text{COOR}_{12}$, in which R_{12} is C_1 - C_{18} alkyl, or at least one copolymer comprising recurring structural units of the formula

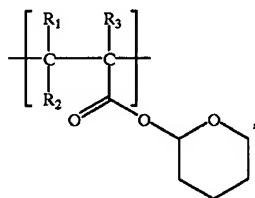


in which R_{15} is phenyl with the proviso that the mean molecular weight (weight average) of the copolymer is 1000-500,000 daltons and the content of carboxyl groups is from 0.40 to 4.00 mol carboxyl groups per kg copolymer,

(c) at least one compound which forms an acid on exposure to actinic radiation, and
(d) an organic solvent.

2. A composition according to claim 1, wherein component (a) is at least one homopolymer or copolymer comprising recurring structural units of the formula Ia in which R_1 and R_2 are hydrogen and R_3 is hydrogen or methyl.

3. A composition according to claim 1, wherein component (a) is at least one homopolymer or copolymer comprising recurring structural units of the formula III



in which

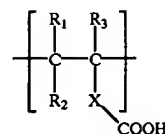
R_1 , R_2 and R_3 , are as defined in claim 1.

4. A composition according to claim 3, wherein component (a) is at least one homopolymer or copolymer comprising recurring structural units of the formula III in which R_1 and R_2 are hydrogen and R_3 is hydrogen or methyl.

5. A composition according to claim 1, wherein component (b) is at least one copolymer comprising 5-40% by weight of recurring structural units of the formula IIa and 95-60% by weight of recurring structural units of the formula IIb

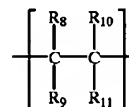
(IIa)

5



(IIb)

10



15 in which R_1 , R_2 , R_3 , R_8 , R_9 , R_{10} , R_{11} and X are as defined in claim 1, with the proviso that the mean molecular weight (weight average) of the copolymer is 1000-500,000 daltons and the content of carboxyl groups is from 0.40 to 4.00 mol/kg.

20 6. A composition according to claim 5, wherein component (b) is at least one copolymer comprising recurring structural units of the formula (IIa), in which R_1 and R_2 are hydrogen, R_3 is hydrogen or methyl and X is a direct bond.

7. A composition according to claim 5, wherein component (b) is at least one copolymer comprising 5-35% by weight of recurring structural units of the formula IIa and 95-65% by weight of recurring structural units of the formula IIb.

8. A composition according to claim 1, wherein component (a) is at least one homopolymer or copolymer comprising 20-100% by weight of recurring structural units of the formula Ia and 80-0% by weight of recurring structural units of the formula Ib.

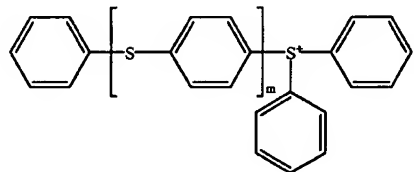
9. A composition according to claim 1, comprising 10-95% by weight of component (a) and 90-5% by weight of component (b), based on the sum of components (a)+(b).

10. A composition according to claim 1, wherein component (c) is a photosensitive diazonium, sulfonium, sulfoxonium or iodonium salt or a photosensitive sulfonic acid ester.

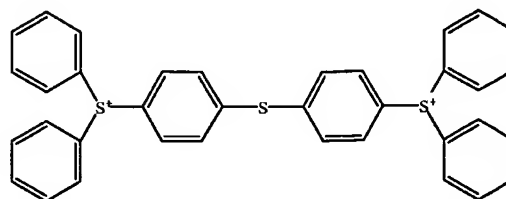
11. A composition according to claim 1, wherein component (c) is triphenylsulfonium tetrakis(pentafluorophenyl)borate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium hexafluorophosphate, triphenylsulfonium hexafluoroarsenate or a hexafluorophosphate or hexafluoroantimonate of the following sulfonium ions:

(III)

50



55



in which m is an integer from 1 to 10.

12. A composition according to claim 1, wherein component (d) is methoxypropyl acetate.

13. A process for the production of relief structures on a circuit board, which comprises coating a substrate with a

19

composition according to claim 1, and exposing the film obtained after removal of the solvent imragewise and subsequently developing the exposed film in an aqueous-alkaline medium.

14. A process according to claim 13, which comprises the following steps:

- (A) coating a copper-laminated substrate with a composition according to claim 1 by application of liquid resists by known methods;
- (B) removal of the solvent by drying at temperatures of 10
from 30° C. to 130° C.;

20

(C) exposure to actinic radiation through a mask or by means of direct laser irradiation;

(D) development using aqueous-alkaline or semiaqueous-alkaline developer solutions;

(E) etching and;

(F) removal of the photoresist coating which remains by stripping.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5, 939,242
DATED : AUGUST 17, 1999
INVENTOR(S) : QIAN TANG ET AL.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the title page, item [30] should read:

-- [30]

Foreign Application Priority Data

| | | |
|------------------|-------------|-----------------|
| June 22, 1994 | Switzerland | 01 992/94-8 |
| January 18, 1995 | Switzerland | 00 138/95-5 --. |

Signed and Sealed this
First Day of February, 2000

Attest:



Q. TODD DICKINSON

Attesting Officer

Acting Commissioner of Patents and Trademarks